OXIDATION OF ISOBUTENE

by

JAMES HAY

Thesis presented for the Degree of Doctor of Philosophy of the University of Edinburgh in the Faculty of Science.

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ABSTRACT OF THESIS

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Summary.

A study has been made of the slow combustion of isobutene in a static system. The reactions were carried out initially in a pyrex glass reaction vessel. Comprehensive product analysis was carried out almost entirely by gas chromatography. The effect on the product distribution of varying the ratio of oxygen:isobutene pressure over a four fold range and of varying the ratio of isobutene:oxygen pressure over the same range was studied at 273°. Similarly, the product distribution was determined for the oxidation of 1:1 mixtures of isobutene:oxygen at a series of temperatures in the range 246° - 352°. Relative activation energies of the reactions producing many of the products were determined.

The early stages of the oxidation produced acetone and formaldehyde as the major products, the two accounting for about 70% of the carbon consumed at low conversions of isobutene. The major products were produced by an apparently homogeneous process involving attack on the olefinic bond of the fuel molecule. A reaction mechanism has been proposed for the formation of acetone and formaldehyde by homogeneous breakdown of intermediate C_4 hydroperoxy radicals formed by addition of hydroperoxy to isobutene.

The wide variation of the initial yields of the variety of minor products of the reaction could not be explaned on the basis of present day theories of slow combustion. The effect on the product distribution of varying the nature of the reaction vessel surface was studied by carrying

Use other side if necessary.

out oxidations in vessels coated with a range of inorganic materials from acidic to basic.

Although the reaction appeared to be of a free radical nature and the pressure/time curves were of a characteristic sigmoid shape, there was no evidence of branching reactions below 300° and products were produced initially at a maximum rate. Above this temperature the product development assumed a more autocatalytic form which has been supposed as being due to oxidation of isobutyraldehyde which was an initial product in this temperature range.

It has been proposed that contrary to general belief the nature of the reaction vessel surface is instrumental in controlling the formation of minor products and that they are produced by heterogeneous decomposition of oxygenated radical species.

The appearance of isobutene oxide and isobutyraldehyde in the reaction products necessitated a separate study of the isomerisation of isobutene oxide to ascertain whether isobutyraldehyde was a legitimate product of the oxidation or formed by isomerisation of the epoxide.

The kinetics of the oxidation were studied at 303° and the variation of kinetic parameters, although still largely unexplained, was found to be in reasonable agreement with the results obtained from previous kinetic studies carried out on the same hydrocarbon.

Several simple reaction mechanisms involving homogeneous and heterogeneous processes have been discussed to illustrate that the relationship between the reaction vessel surface and the formation of minor products is not a simple one.

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SECTION A

INTRODUCTION

1. INTRODUCTION

In a paper presented in 1892 in the Journal of the Chemical Society, W. A. Bone gave a historical résumé of the work carried out on slow combustion in the nineteenth century, in which he accredited Dalton with the first oxidation of ethylene in 1807. Since 1892, the history of slow combustion reactions in general has been greatly influenced by the application of new theories of oxidation and more sophisticated experimental techniques. As a result of this, the period 1892 to the present time is divided into three distinct eras.

The divisions were brought about by (a) the development of the theory of chain reactions culminating, in the late nineteen twenties and early thirties, in the theoretical postulations of Semenoff,[1] and (b) the advent in the early nineteen fifties of gas chromatography which gave a much more refined and adaptable analytical tool for kinetic work than ever before.

Although the work on combustion of hydrocarbons spans over a hundred and fifty years, there are still many aspects of these reactions largely unexplained and, with olefins especially, there is still much controversy as to the exact nature of the initial reaction.

This dissertation is concerned principally with the gas phase

oxidation of olefins. It has, however, proved almost impossible to restrict the text to such a narrow field, especially in the introduction, so, although this subject provides the main theme of the first few sections, the environment in which such reactions developed has been exemplified by reference to related combustion systems.

1.1. Historic Review - Before 1935.

Armstrong[2] was the first to suggest that hydrocarbon oxidation involved stepwise degradation of the fuel molecule via hydroxylated intermediates. The first serious experimental verification of this idea, however, came from Bone[3] in the late nineteenth and early part of the twentieth centuries although a communication by Schutzenberger[4] had been made on the production of formaldehyde by passing oxygen and excess ethylene through a glass tube at 400°.

The initial olefin work in both static and flow systems[5] was done almost exclusively on ethylene. Bone concluded that the combustion of a hydrocarbon was essentially a process of hydroxylation, oxygen being distributed between the carbon and hydrogen of the fuel molecule, giving rise to unstable hydroxylated molecules which, sooner or later, depending upon prevailing experimental conditions, suffered thermal decomposition to simpler products. The main course of the combustion of ethylene being represented as follows:

$$CH_2{:}CH_2 \longrightarrow \underset{\text{stage 1}}{CH_2{:}CH.(OH)} \longrightarrow \underset{\text{stage 2a}}{(HO).CH{:}CH.(OH)} \longrightarrow 2H.CHO$$

$$\underset{\text{stage 2b}}{H.CHO} \xrightarrow{CO+H_2} \underset{\text{stage 3}}{(HO).CHO} \xrightarrow{CO+H_2O} \underset{\text{stage 4}}{(HO)_2.C{:}O} \longrightarrow H_2O+CO_2$$

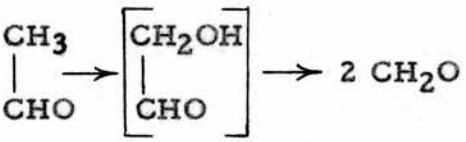
At low temperatures, (250° - 400°), formaldehyde was the main intermediate. The stage at which secondary decompositions set in was determined entirely by the temperature of the reaction. Below the ignition temperature, such changes did not occur to any serious extent until stage 3. The greater part of the formic acid then decomposed into carbon monoxide and steam whilst the remainder was further oxidised to carbonic acid (stage 4), which in turn went to carbon dioxide and steam.

This theory established the formation of aldehydes prior to products of complete combusion, i. e. carbon oxides and steam, but suffered from the weakness that the vinyl alcohol, the primary intermediate, was not detected. The evidence pertaining to the existence of the intermediate alcohol was the detection of its isomer acetaldehyde and the fact that, in the explosive combustion of ethylene, [6] experiments conducted with insufficient oxygen for complete combustion, (which would yield carbon monoxide and hydrogen), gave steam and acetylene. It was concluded that the normal chain of reactions leading to carbon monoxide and hydrogen via dihydroxy ethylene could not occur with insufficient oxygen. Instead, the monohydroxy ethylene decomposed to acetylene and steam.

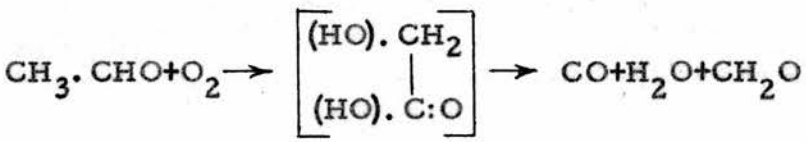
Bone further postulated that at high temperatures and with sufficient oxygen present, i. e. in the explosion wave, the initial stage of the combustion involved direct introduction of the oxygen molecule into the hydrocarbon, giving a direct passage from ethylene to dihydroxyethylene

as a result of collisions between single molecules of oxygen and ethylene. His theory therefore predicted no discontinuity between slow and rapid combustion.

Blair and Wheeler,[7] using a flow system, found appreciable quantities of acetaldehyde and formic acid according to the proportion of oxygen present and they suggested that, under the conditions of slow combustion of their experiments, acetaldehyde and not dihydroxyethylene was produced as the main intermediate. Since the reaction produced greater than 50% formaldehyde, this scheme was compatible with Bone's theory only if acetaldehyde then oxidised as follows:



and not as Bone and Stockings[8] had predicted:



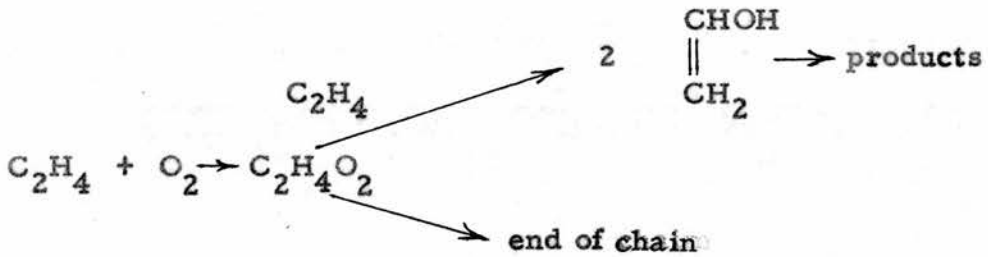
The first serious doubts of Bone's theory came from Hinshelwood and Thompson[9] who studied the oxidation of ethylene between 400° - 500° and observed

(a) a great influence by initial pressure variations on the reaction rate,

(b) increasing the surface area retarded the reaction and

(c) the rate was virtually independent of oxygen pressure, but varied as the third power of the ethylene pressure. They concluded

that oxidation must occur by a chain process. The addition of inert gas, apart from shortening the induction period, had little effect upon the reaction rate suggesting that the chains must be short. Hinshelwood favoured the suggestion of Egerton and Gates [10] that the initial process was the formation of an unstable peroxide which provided active centres from which the chains could proceed:

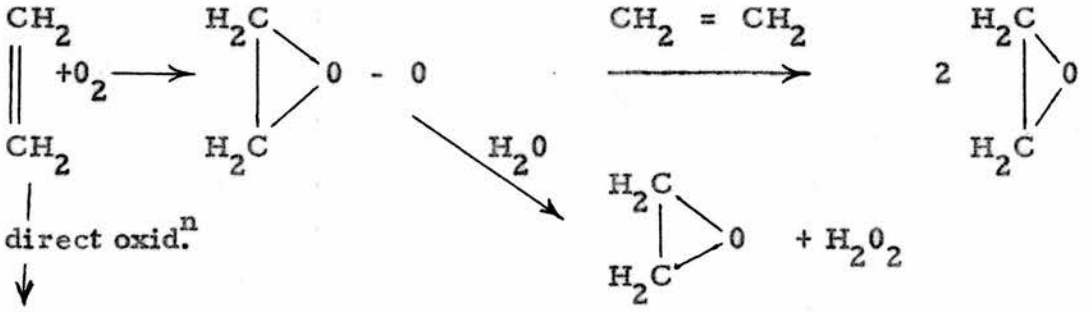


Some evidence had already beengiven for the formation of addition complexes or peroxides by the action of oxygen on substances containing a double bond. [11] It should be noted that Hinshelwood still favoured the formation of an alcoholic intermediate. The divergence from Bone's theory lay in the initial formation of a peroxide.

Lenher [12] studied ethylene oxidation in a flow system over a variety of temperatures, contact times and concentration variations, and agreed that the great dependence of the reaction rate on ethylene concentration and independence of oxygen concentration suggested that the reaction chains were propagated through collision of a primary reaction product (peroxide) with ethylene in accordance with similar observations in the oxidation of acetylene, [13] benzene, [14] and hydrogen. [15]

Lenher's reactions gave, in addition to the accepted products of formaldehyde, formic acid, carbon oxides and steam, appreciable quantities of ethylene oxide under all conditions, and small amounts of glyoxal and dioxymethyl peroxide ($CH_2OH.OO.CH_2OH$) depending upon conditions. Hydrogen peroxide was also detected.

Slow thermal oxidation of propylene under similar conditions gave a peroxide thought to be analogous to dioxymethyl peroxide in the ethylene oxidations, also propylene oxide, glycol and aldehyde plus acetic acid, acetaldehyde and formaldehyde. The occurrence of formaldehyde and epoxide in the early stages of reaction provided evidence that the formation of both of these compounds was the primary step in the oxidation. The formation of hydrogen peroxide could then conceivably arise from the action of water on the initially formed peroxide, in accordance with the behaviour of organic peroxides[16]. Pease[17] had also detected hydrogen peroxide in the combustion of hydrogen at 550°.



The controversy now raging as to the nature of the initial intermediate led Bone[18] to a further investigation of the oxidation under better controlled conditions. His theory had been weighted by Newitt and

Haffner [19] and Pichler and Reder [20] who had detected methyl alcohol in the products of methane and ethylene combustions respectively.

The reinvestigation at 300° and atmospheric pressure substantiated his view that the initial intermediate was a vinyl alcohol and not a peroxide. Any accumulation of the alcohol would be rapidly transformed into an equilibrium mixture of the three C_2H_4O isomers i.e., alcohol, aldehyde and epoxide, the prevailing oxidation conditions controlling the equilibrium mixture. He also established that the course of the oxidation was unaffected by the presence of water vapour which Armstrong [21] had thought to be the oxygen 'carrier'.

The position in 1935.

It was agreed at this time that the gas phase oxidation of ethylene, so far the only olefin studied in detail, proceeded by a homogeneous chain mechanism, (the chains probably being short), the rate being very dependent upon initial hydrocarbon pressure but almost independent of oxygen pressure.

The main disagreement was the exact nature of the initial reaction.

The value of the early work lay in the fact that the hydroxylation theory of Bone provided a stepwise reaction mechanism which explained all the analytical features of a type of reaction which at first seemed simple but since proved to be extremely complex.

The shortcomings of the theory were its inability to explain several

kinetic features of the reaction e. g. the autocatalytic nature, action of catalysts and inhibitors, inhibition of the slow combustion by increasing the surface area, the effect of variation of reaction vessel diameter on the ignition temperature.

It was realised, however, that the peroxide theory also had limitations, e. g. the addition of inert gas increased the rate of reaction whereas it would have been expected to decrease due to more unprofitable collisions occurring, also only small amounts of peroxide were detectable during the induction period, the supposed time of peroxide build up.

The final rejection of the hydroxylation theory came partly from Bone's own evidence.[22] He found that, during the oxidation of methane, methyl alcohol oxidised much faster than methane and formaldehyde much faster than either. Newitt and Gardner[23] found that the ratio of methyl alcohol to formaldehyde never exceeded O. 3, a stationary state ratio far too low to uphold the hydroxylation theory.

1.2 Development and Application of Chain Mechanisms

The beginning of a new era in gas phase hydrocarbon combustion came about in the early nineteen thirties by the introduction of chain mechanisms involving reactive intermediate species, instrumental in the formation of products, and regenerated to continue the chain reaction many times before their ultimate destruction.

The concept of chain reactions was not new at this time. It had been put forward by Bodenstein[24] to account for the high quantum yield in the photochemical reaction between hydrogen and chlorine. He proposed chains involving electrons. This was later modified by Nernst[25], who proposed an atomic chain for the same reaction.

$$Cl + H_2 = HCl + H$$

$$H + Cl_2 = HCl + Cl$$

In order to interpret the speeds of some first order reactions, Christiansen[26,27] proposed energy chains where molecules of reaction products, just after reaction, were considered to contain an excess of energy sufficient to activate molecules of reactant at their first encounter. The subsequent reaction products would also have excess energy and so the chain would be continued until deactivation of a 'hot' product molecule by unfruitful collisions. The ready application of energy or thermal chains to the explanation of the phenomenon of negative catalysis[26] added substance to the theory. It was thought that the negative catalyst or inhibitor was able to

react with one of the links of the chain, consequently breaking the chain and thus lowering the reaction rate.

Direct evidence of the existence of chains in the hydrogen chlorine reaction came from Weigert and Kellerman[28] who showed that the extent of chemical change, measured by changes in refractive index caused by the heat of reaction, did not develop to its full extent for a fraction of a second after momentary illumination, showing that the light set up a chain of processes which continued independently in the dark.

Backstrom[29] strengthened the concept of thermal chains by studying the photochemical oxidation of benzaldehyde and heptaldehyde. He observed large quantum yields, (10,000 and 15,000 respectively), and the reactions were markedly subject to inhibitor action. Also, the corresponding reactions which took place in the dark were subject to the influence of the same inhibitors in an almost exactly parallel way.

Hinshelwood and Thompson[30] and Gibson and Hinshelwood[31] investigated the hydrogen-oxygen reaction in a static system, and accounted for the inhibitory effect of the walls of the reaction vessel at certain temperatures as being due to the breaking of the thermal chains by the energised product molecules colliding with, and coming into thermal equilibrium with the walls.

Although Hinshelwood considered the hydrogen-oxygen system to be a thermal chain process, Bonhoeffer and Haber[32] believed that it proceeded by

a free radical chain process. However, this idea was not accepted until later.

The application of chain theories to hydrocarbon oxidation came first from Norrish[33] in 1935 in an attempt to explain the kinetic data of the time. He proposed an "atomic chain hypothesis" involving oxygen atoms and free radicals derived from the hydrocarbon fuel molecule, the scheme for ethylene being represented:

Initiation

$$C_2H_4 + O_2 = 2\,CH_2O \quad - \quad (1)$$

$$CH_2O + O_2 = H.COOH + O \quad - \quad (2)$$

Propagation

$$\begin{cases} C_2H_4 + O = CH_2O + CH_2 \\ CH_2 + O_2 = CH_2O + O \end{cases}$$

Termination

$$O + C_2H_4 + X \xrightarrow{\text{wall}} C_2H_4O + \tfrac{1}{2}O_2 + X$$

Reaction (2) was envisaged as the branching reaction leading to explosion at higher temperatures.

The essential difference between the theories of Norrish and Bone lay in the fact that, in the latter, the aldehyde was formed by way of an intermediate alcohol whereas, in the former, the aldehyde was formed as a direct product of the chain propagating step.

An alternative reaction scheme citing hydroperoxides as the product of the propagation step and aldehydic products as a result of a branching reaction was suggested by Ubbelohde[34]. The initiation process in this

case was visualised as the production of an alkyl radical by action on the fuel of an $R.CO_3$ radical, this species having been originally suggested by Backstrom following investigation of aldehyde oxidations:

Initiation

$$R.\overset{\overset{00}{|}}{C} : 0 \quad + \quad R.CH_3 \quad = \quad R.\overset{\overset{00H}{|}}{C}. : 0 \quad + \quad RCH_2$$

Propagation

$$\begin{cases} R.CH_2 \quad + \quad 0_2 \quad = \quad R.CH_200 \\ R.CH_200 \quad + \quad R.CH_3 \quad = \quad R.CH_200H \quad + \quad R.CH_2 \end{cases}$$

Branching

$$R.CH_2.00H \quad = \quad R.CH_20 \quad + \quad 0H$$

This scheme was similar to Norrish's in that it involved a chain reaction in the propagation step and had the advantage that this step involved molecular rather than atomic oxygen. The essential difference was the formation of a hydroperoxide as opposed to an aldehyde in the propagation step.

The principle of the two theories, with slight modification, laid the basis for all future hydrocarbon oxidation mechanisms.

1.3 Branching and Degenerate Branching Chains

A non branching reaction occurs where each free radical taking part in any step of a reaction chain gives rise to one other radical and a stationary or steady process occurs when there is an equilibrium set up between the number of radicals initiated and the number destroyed.

On the other hand, a propagation step may involve the production of two or more active centres from one, each new centre being capable of initiating a fresh chain. In this way, there may be a slow or rapid build up of free radicals in the system, depending upon experimental conditions, the latter condition leading to explosion.

For example, reactions (1a) and (1b) represent a steady non-branching reaction, while reactions (2a) and (2b) represent a highly branching reaction which would lead to explosion.

$\underline{H} + Cl_2 = HCl + \underline{Cl}$ ----- (1a) radicals underlined

$\underline{Cl} + H_2 = HCl + \underline{H}$ ----- (1b)

$\underline{H} + O_2 = \underline{OH} + \underline{O}$ ----- (2a)

$\underline{O} + H_2 = \underline{OH} + \underline{H}$ ----- (2b)

Semenoff[1] calculated for the rates of branching reactions an expression which was later represented by Hinshelwood[35] as

$$v = \frac{F}{fs + fg + A(1-\alpha)}$$

where v = reaction rate

F represents the rate of chain initiation

fs, fg are the rates of destruction of the radicals at the surface and in the gas phase respectively.

A is a function of the chain branching process

α = the number of active particles resulting from one original active particle involved in the propagation of the chain.

If there is chain branching, α is greater than unity so that the term $A(1 - \alpha)$ becomes negative; and if the magnitude of this negative term is such that it just balances the term (fs + fg), the rate becomes infinite and explosion occurs, i.e. there may be a sharp transition from a stationary state to a non stationary state. The relative magnitudes of (fs + fg) and $A(1 - \alpha)$ depend upon the concentrations of the various molecules. The denominator may therefore be positive for certain concentrations and negative for others. At any particular set of conditions for which $fs + fg + A(1 - \alpha)$ equals zero, there occurs an explosion limit.

Explosion limits of this type are well defined in the hydrogen-oxygen system[36].

The oxidation of hydrocarbons are generally characterised by three features:

a) an induction period followed by a period of slowly increasing rate until a maximum rate is reached, or the reaction becomes

unstable.

b) the occurrence of explosion limits.

c) the occurrence of cool flames under certain conditions of temperature and pressure.

Primarily in order to explain a), Semenoff developed the chain theory further to include 'degenerately branching chains'. That chain branching does occur is indicated by the fact that the reactions accelerate without any rise in temperature although the branching must be such that it occurs only infrequently. Semenoff proposed that an intermediate product was formed which, although normally inert, could, on occasion, undergo a reaction to produce a free radical.

$$\text{Hydrocarbon} \rightarrow \text{Intermediate} \begin{cases} \nearrow \text{Stable molecule} \\ \searrow \text{Free radical} \end{cases}$$

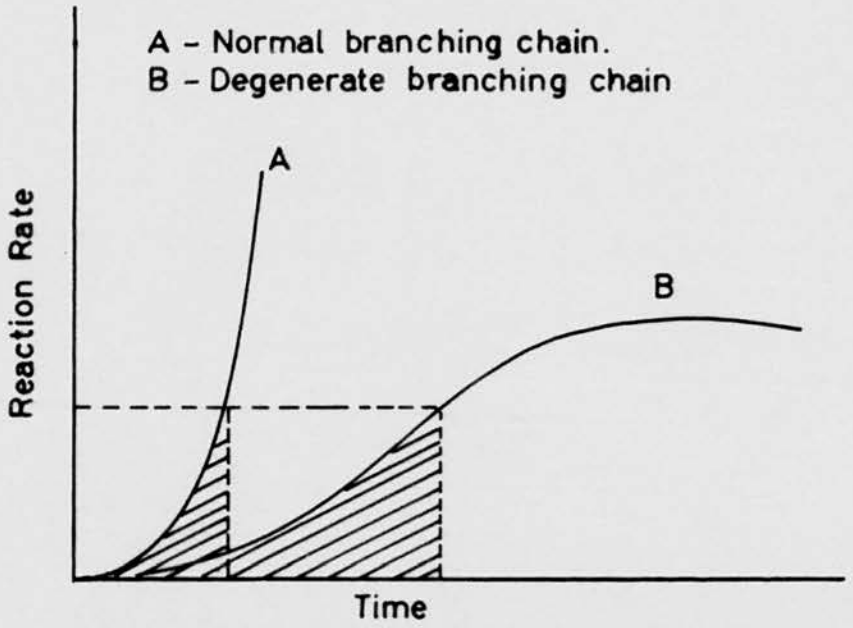
The intermediate he proposed would have a fairly long life so that branching was delayed. This adequately explained the existance of an induction period as a period of time when the intermediate accumulated with a slow build up of radicals until sufficient were present to cause acceleration.

With hydrogen-oxygen mixtures, branching chains give rise, under isothermal conditions, to infinite velocity whereas with hydrocarbons the number of radicals grows so slowly that before the rate becomes infinite the effect of the removal of reactants is significant and the rate slowed down.

A graphic representation of the variation of reaction rate with time for normal and degenerately branching chain reactions is shown in Fig.A.1. The nature of the intermediates leading to degenerate branching will be considered in a later section.

Figure A.1.

Variation of reaction rate with time.

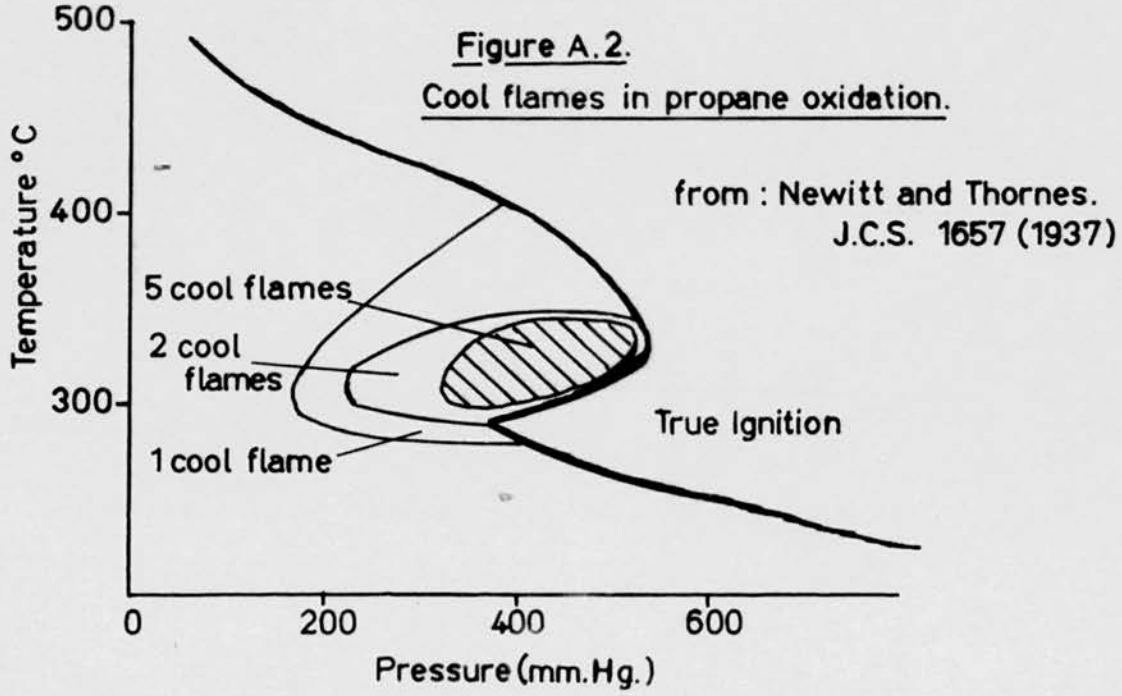


(Reproduced from 'Chemical Kinetics and Chain Reactions.' p.73.
- Semenoff. 1935.

Figure A.2.

Cool flames in propane oxidation.

from : Newitt and Thornes.
J.C.S. 1657 (1937)



1.4 Cool Flames

Cool flames are explosions of the degenerately branching type, the reaction velocity being high but not infinite. The cool flames are probably thermally controlled explosions which are quenched because of a change in the reaction mechanism above 400° so that they never take off into real explosions. It is supposed in hydrocarbon combustion that true explosions, when they occur, are of the thermal type due to self heating of the mixture.

Cool flames are characterised by sudden changes in pressure during the course of the oxidation and by the appearance of luminescence caused by electronically excited formaldehyde[37]. The temperature and pressure limits for the occurrence of cool flames and explosions have been studied by Townend[38]. A graphical representation of the cool flame and explosion limits for propane oxidation[39] is given in Figure A.2.

For all hydrocarbons, the temperature limits for the onset of cool flames are approximately 280° - 410°, true explosion occurring at higher temperatures if the pressure is high enough. The existence of an explosion peninsula between two temperature limits contrasts with the hydrogen-oxygen systems where the explosion region is confined by two pressure limits.

The upper and lower limits of explosions can be adequately explained by the degenerate branching hypothesis. The lower limit occurs because degenerate branching becomes less important as the temperature is lowered and eventually becomes too slow to allow the number of radicals in the system

to increase. The upper limit is ascribed to the fact that there is some chain breaking process which competes with the degenerate branching and becomes relatively more important as the temperature is raised.

1.5 Theories of Degenerate Branching

With the final developments of a chain theory which could explain the kinetic and analytical features of slow combustion, one of the remaining points of disagreement was the actual nature of the degenerate branching agent. It was agreed that aldehydes acted as the agents of degenerate branching above 400° but, for reactions at lower temperatures, opinions were equally divided between aldehydes and peroxides as the branching species. The most attractive feature of the peroxide theory was the fact that fission of an O-O bond in an intermediate peroxide or hydroperoxide could readily explain the formation of major products containing only one oxygen atom.

Unfortunately, little work was done on gas phase olefin oxidation during the period 1935-50 so the controversies regarding intermediates were based mainly on work carried out on alkanes. However, the general principles of the two theories of the time, the aldehyde and peroxide theory, were later to be applied to olefins as well.

The Peroxide Theory

Ubbelohde[34] was the first to cite peroxides as degenerate branching agents in low temperature hydrocarbon oxidation. He postulated that hydroperoxides were formed in the propagating steps of the reaction and that these would subsequently decompose into free radicals with a resultant branching of the chain reaction:

$$\text{Propagation} \begin{cases} R.CH_2. + O_2 = R.CH_2.OO \\ R.CH_2.OO + R.CH_3 = R.CH_2OOH + R.CH_2. \end{cases}$$

$$\text{Branching} \quad R.CH_2.OOH = R.CH_2O + OH$$

There was no doubt that in liquid oxidations, where the reaction temperature was much lower than in gas reactions, peroxides were the main intermediates responsible for degenerate branching[40] and the kinetics of olefin oxidations of substances with an α methylenic hydrogen atom could be comprehensively covered by the reation scheme.[41]

Initiation: Production of R. or $RO_2.$

$$\text{Propagation:} \begin{cases} R. + O_2 = RO_2. \\ RO_2. + RH = RO_2H + R. \end{cases}$$

$$\text{Termination:} \quad \left.\begin{array}{l} 2R. \\ 2\ RO_2. \\ R. + RO_2. \end{array}\right\} \rightarrow \text{non initiating or propagating products}$$

Cullis and Hinshelwood[42], and Egerton and Young[43], showed that during the gas phase oxidation of hydrocarbons at 200° - 300° the peroxide content of the product mixture rose to a maximum and then decreased, the maximum occurring close to the time at which the maximum rate of pressure change occurred.

Mulcahy[44] studied similar reactions under the same temperature conditions and found good agreement between the kinetics of the gas phase oxidations and those observed by Bolland[41] in the liquid phase reactions.

Catalytic oxidations have also provided sufficient evidence of the presence of peroxides in oxidation systems, the use of a catalyst inducing reaction below 200°. Bawn, Pennington and Tipper[45] found that in the early stages of the cobalt catalysed liquid oxidation of 2 - methyl but -2-ene, the corresponding hydroperoxide was present in an equilibrium concentration given by $[ROOH] \propto [RH]^2$, and, under certain conditions, 75% of the absorbed oxygen was present as hydroperoxide.

Rust and Vaughan[46] investigated the hydrogen bromide catalysed oxidation of isobutane and obtained similar yields of t-butylhydroperoxide from a 10:10:1 mixture of isobutane: oxygen: hydrogen bromide. The same workers had also examined the photochemical oxidation of ethylene, propylene[47], and straight chain paraffins up to C_4[48], catalysed by hydrogen bromide and found that only hydroperoxides of the higher hydrocarbons were obtained, none being detected in the C_2, C_3 systems[49].

It should be noted that experimental techniques used for the detection of peroxides before the development of paper chromatography for this purpose[50] would not satisfactorily differentiate between hydrogen peroxide, hydroperoxides and other oxidising materials, and some of the results in this respectshould be accepted with reservation.

It had been thought too that the nature of the radical R. in intermediate peroxides would account for the different rates of oxidation of some hydrocarbons from others[51, 52]. However, it has since been shown that

the rates of decomposition of the lower alkyl hydroperoxides are not greatly different.[53]

Cartlidge and Tipper[54] used paper chromatography to detect and isolate the hydroperoxides formed in the oxidation of propane at 327°, n-heptane at 250° - 270° and n-butane at 315° - 345°, and found that the peroxidic material isolated from the n-butane, and n-heptane oxidations, (which was greater than the free aldehyde), consisted of a mixture of hydroperoxide, hydrogen peroxide and hydrogen peroxide - aldehyde adducts. With propane, however, the peroxides produced consisted mainly of hydrogen peroxide. Cartlidge and Tipper concluded that hydroperoxides could not be the agents of degenerate branching in lower hydrocarbon systems, although these substances could possibly act as such agents in the higher hydrocarbon-oxygen systems.

This view was supported by Kirk and Knox[55], who found that at 318° the lifetimes of the ethyl and propyl hydroperoxides were too short for them to function as degenerate branching agents in the ethane and propane oxidations above 300°. Nevertheless, higher hydroperoxides, if formed, would cause chain branching, since at least a proportion would decompose homogeneously giving radicals.

The most recent work on low temperature catalytic oxidation, on isobutane[56] and isobutene[57], has shown that below 200° the branching reaction seems to be bimolecular between R00H, and hydrogen bromide, the

hydroperoxide arising from abstraction of a hydrogen atom from hydrogen bromide by the peroxy radical, (RO_2.).

Direct evidence that peroxides are not the agents responsible for degenerate branching has been given by Batten and Ridge[58] who found that withdrawing the reaction mixture from the reaction vessel during the induction period, destroying the peroxidic material by allowing the mixture to stand in contact with mercury, and then replacing the mixture in the reaction vessel, caused no change in the rate of the subsequent reaction.

Destruction of peroxides during oxidation reactions had been carried out by other workers to demonstrate that these compounds were not the agents of degenerate branching. Shtern and Polyak[59], and Shtern[60], used the above method in the oxidation of propane and propylene while Pease[61] destroyed the peroxides in the oxidation of propane by coating the reaction vessel with potassium chloride.

The large amount of work carried out on peroxides in order to determine their role in branching reactions gave no unambiguous indication as to the exact part they played in these reactions. In the next section, the merits of the aldehyde theory will be developed.

Aldehyde Theory

The importance of aldehydes as intermediates in hydrocarbon oxidation was first noted by Pope, Dykstra and Edgar[62] in 1929. They studied the oxidation of isomeric octanes and postulated that the oxidation

occurred thus:

$$R.CH_2.CH_3 + O_2 = R.CH_2.CHO + H_2O$$

the aldehyde formed being degraded:

$$R.CH_2.CHO + O_2 = R.CHO + CO + H_2O$$

and the degradative scheme continued until the final production of formaldehyde. This theory, as such, was rejected since one would have expected to have been able to detect all the intermediate aldehydes between $R=CH_3.(CH_2)n$ and $R=CH_3$, as well as formaldehyde, a fact not observed experimentally. Also, formaldehyde produced by such a scheme would not be in an excited state as required for cool flame formation.

Lewis and von Elbe[63] overcame the objections to a straight run through successive aldehydes by modifying Pope's scheme to a degradation of radicals rather than molecules:

$$R.CH_2CO + O_2 = R.CO + CO + H_2O = CH_3CO + CO + H_2O$$

By further postulating a different reaction for the acetyl radical than for the higher radicals:

$$CH_3CO. + O_2 = CH_2O + CO + OH$$

they could explain the formation of excited formaldehyde since this reaction would be exothermic by over 100 k. cal. (Note: Modern thermochemical data applied to this reaction gives ΔH = -69 k. cal. which does not in fact account for formaldehyde in an excited state). However, the fate of acetyl radicals at the temperatures of hydrocarbon oxidations is more likely to be:

$$CH_3.CO = CH_3. + CO$$

even if the higher carbonyl radicals were stable enough to continue such a chain.

Norrish[64] proposed a reaction scheme based on aldehydes:

Propagation:
$$\begin{cases} R.CH_2.CH_3 + OH = R.CH_2.CH_2 + H_2O \\ R.CH_2.CH_2 + O_2 = R.CH_2.CHO + OH \end{cases}$$

Branching:
$$R.CH_2.CHO + O_2 = R.CH_2.COOH + O$$

Degradation:
$$R.CH_2.CHO + OH = R.CH_2. + CO + H_2O$$
$$R.CH_2 + O_2 = R.CHO + OH$$
$$R.CHO + OH = R. + CO + H_2O$$

The essential difference between the aldehyde and peroxide theories lay in the stability of the peroxy radical. Norrish considered this radical to have only a fleeting existence, decomposing rapidly into an aldehyde and a hydroxyl radical. On the other hand, protagonists of the peroxide theory i.e. Ubbelohde, Hinshelwood, Walsh etc., considered that the radical existed long enough to be able to abstract a hydrogen atom from the hydrocarbon fuel molecule.

$$R.CH_2.OO \xrightarrow{RH} R.CH_2.OOH \qquad \text{Peroxide Theory}$$
(stable)

$$R.CH_2. + O_2$$

$$R.CH_2.OO \longrightarrow R.CHO + OH \qquad \text{Aldehyde Theory}$$
(unstable)

Just as peroxides are detected at early stages in oxidation systems, there is evidence for maximum aldehyde concentrations at, or near, the time of

of maxiimum rate of oxidation.[65] Both aldehydes and peroxides in small quantities shorten the induction periods.[58,66]

From the evidence available it would appear that, in oxidations below 200°, the branching agent is a peroxide, normally a hydroperoxide, while above 400° it is an aldehyde. In the intermediate range, however, at least up to 350°, both aldehydes and peroxides probably influence the branching characteristics of the oxidation, and, although it is unlikely that the effect of one or other can occur exclusively, the reaction conditions e.g., surface/volume ratio, fuel/oxygen ratio, and the condition of the reaction vessel surface, may influence the relative importance of each type of branching agent.

The fact that in many oxidation systems the amounts of aldehydes and peroxides formed were small compared to the amounts of fuel consumed raised the possibility of alternative paths for the peroxy radical, i.e.

$$R. + O_2 \rightarrow [RO_2] \rightarrow R.CHO + OH \quad \text{'Aldehyde'}$$
$$\searrow \text{other products}$$

$$R. + O_2 \rightarrow RO_2 \rightarrow ROOH \quad \text{'Peroxide'}$$
$$\searrow \text{other products}$$

1. 6. Nature of the propagating radical.

As yet there is no direct evidence pertaining to the exact nature of the propagating radical in hydrocarbon oxidations but indirect evidence suggests OH or HO_2.

Both hydroxyl and hydroperoxy radicals have been observed mass spectroscopically in the hydrogen-oxygen system [36, 67] and the enhanced rate of this reaction in a boric acid coated reaction vessel was proposed by Baldwin and Mayor [68] as being due to preservation of hydroperoxy radicals.

Norrish incorporated hydroxy radicals as the propagating species in his 'Aldehyde Hypothesis' (see page 26), and Walsh [69] favoured OH as the chain carrier in the oxidation of methane. This was supported by McKellar and Norrish [70] after study of the flash photolysis of methane, oxygen, nitrogen dioxide mixtures which suggested that the primary process was :

$$CH_3. + O_2 = CH_2O + .OH$$

Hydroperoxy radicals were first suggested by Marshall [71] to explain the mercury photosensitised reaction between hydrogen and oxygen. The same radical was considered to be the radical chain breaking species in the second explosion limit of the thermal oxidation of hydrogen [72] and was detected mass spectroscopically in the reaction between hydrogen atoms and oxygen molecules. [73, 74]

The high yields of olefins obtained during alkane oxidations at temperatures above 400° led to the conclusion that oxygen could abstract a hydrogen atom from an alkyl radical with the resultant formation of an olefin and HO_2.[75-80]

$$R. + O_2 = R' + HO_2$$ where R. = alkyl radical and R' = olefin.

This was established also for the low temperature oxidation of propane[81] and, more recently, ethane[82]. This evidence conflicts with the view that OH is the propagating radical since at least 80% of the alkyl radicals are now known to form HO_2. Thus, if OH attacks RH, HO_2 must somehow be converted to OH. There is no accepted reaction for doing this at temperatures in the region of 300° although, at temperatures above 450° the following reaction may occur:[83]

$$2HO_2 = H_2O_2 + O_2 = 2OH + O_2$$

Knox, Smith and Trotman-Dickenson[84] investigated the competitive oxidation of ethane and propane between 274° and 495° and found that the oxidation rates of the two hydrocarbons were approximately the same, although in isolated systems propane oxidised much faster than ethane. They concluded that the competitive oxidation must have been propagated either

(a) by the same radical over the whole temperature range,

or (b) by different radicals having approximately the same

properties, and that the differences in individual reactivities were due to differences in the rates of processes other than chain propagation.

From the relative rate constants it was deduced that such a radical would have about the same reactivity as a chlorine atom. Since D [H-OH] = 118 k. cal. and D [H-Cl] = 103 k. cal. while D [H-OOH] = 87 k. cal., the overall kinetics suggested OH as the propagating species. However, the formation of propylene and the absence of hydrogen in the early stages of reaction made the only acceptable scheme:

$$C_3H_7 + O_2 = C_3H_6 + HO_2$$

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2$$

: despite the fact that the hydrogen abstraction reaction must be endothermic[85].

There is excellent evidence that hydroperoxy radicals are the propagating species in alcohol oxidations. Bell and Tipper[86] deduced from the effect of surface and inert gas that in the oxidation of methyl alcohol HO_2 radicals were involved in the propagation and termination processes:

$$CH_3OH + HO_2 = H_2O_2 + CH_2OH$$

$$CH_2OH + O_2 = CH_2O + HO_2$$

A study of the oxidation of higher alcohols[87] added support to this reaction scheme. For example, in the oxidation of ethyl alcohol,

Cullis and Newitt found that acetaldehyde and hydrogen peroxide, in equimolar amounts, were the only initial products in the early stages. Also, isopropyl alcohol yielded equimolar quantities of acetone and hydrogen peroxide.

Although the presence of HO_2 radicals has been confirmed in a wide number of oxidation systems, there is still no exact knowledge of the lifetime of the radical in conditions comparable to that existing in hydrocarbon oxidations, apart from the estimated value of about one second by Lewis and von Elbe[72].

From the preceding evidence of the presence of HO_2 radicals in oxidation systems, it seems highly probable that this species will occur in olefin-oxygen systems around 300°.

Since hydrocarbon oxidations take place at lower temperatures than those at which pyrolysis occurs, the initiation reaction must involve a fuel molecule and an oxygen molecule. This reaction must lead to the formation of radicals either by abstraction or addition and may take place at the surface.

Once the reaction gets under way, the contribution of chain carriers from the initiation process will become negligible and virtually all the radicals propagating further chains will be derived from propagating and branching reactions, and may well be a complex mixture of radicals, the two most likely fuel attacking species being OH and HO_2.

In alkane oxidation, it seems unlikely that two such radicals could

exist in comparable quantities since the main propagating step is hydrogen abstraction, and the more reactive OH radicals would be quickly replaced by HO_2:

$$R.CH_2.CH_3 + OH = R.CH_2.CH_2. + H_2O$$
$$R.CH_2.CH_2. + O_2 = R.CH{:}CH_2 + HO_2$$

In olefin oxidation, however, radical addition to the double bond takes place to a much greater extent than hydrogen abstraction. For example, Steacie [88] has shown that radical additions to propylene require an activation energy of only a few k. cal. $mole^{-1}$ whereas abstraction reactions involve a much higher activation energy. Also, Cvetanovic [89] found that oxygen atoms, produced by mercury photosensitised decomposition of nitrous oxide, reacted over twenty times as quickly with ethylene as with n-butane, the initial step with the olefin being addition to the double bond. In the oxidation of ethylene at 400°, Harding and Norrish [90] found that ethylene oxide was produced to the extent of 50% of the formaldehyde. The formation of the oxide cannot be explained unless C-H bonds are assumed to remain intact.

Therefore, selective removal of the hydroxyl radicals by hydrogen abstraction in an olefin system would not occur to the same extent as in alkane oxidations and there is a possibility that the concentration of the two species might be comparable.

Nevertheless, the probability of such a condition does not seem likely since, in alkane oxidations, the kinetics of the ensuing olefin

oxidation are strongly dependent upon the prevailing oxidation of the paraffin and therefore most likely to be suffering attack by the same species, (HO_2 above). Further, once the reaction gets under way there will be a diminution in the hydroxyl radical concentration due to its higher abstracting power of hydrogen atoms from reactive intermediates such as aldehydes.

1.7 Kinetic Parameters in Olefin Oxidation

In ethylene oxidations, pressure time curves for the reaction carried out in a static system at temperatures about 300° are characterised by an initial pressure decrease followed by an increase in pressure to the maximum rate after which the rate of pressure change falls gradually to zero[18,82]. With excess oxygen, or at temperatures greater than 350°, the initial pressure decrease is removed[9,18,90] and the reaction proceeds with a continual increase in pressure.

The oxidation of higher olefins at about 300° shows the same characteristics[90,91,93]. The magnitude of the pressure decrease, the overall pressure increase, and the maximum rate of pressure change, are all strongly dependent upon the initial reactant pressures. In the oxidation of isobutene, Skirrow and Williams[94] found that the extent of pressure decrease became greater, and the overall pressure increase smaller, as the ratio of olefin: oxygen was increased, but at low ratios, the value of the overall pressure increase passed through a maximum. Under conditions of high olefin: oxygen ratios, the overall pressure change became negative, indicating a decrease in the total number of molecules in the system. The effect of lowering the temperature was to reduce the maximum rate of pressure change and lower the overall pressure change during the reaction. The maximum rate of pressure increase passed through a maximum as the initial pressure of fuel was increased and increased steadily with increasing initial oxygen pressure (see also[91, 92]).

The overall pressure changes in olefin-oxygen systems are small compared with the total initial pressure of reactants e.g. in the oxidation of but-2-ene, Blundell and Skirrow[91] measured a total pressure change of 3mm.Hg. from a starting pressure of 72mm.Hg.

Due to the complex nature of the pressure changes, the change of pressure with time cannot normally be used as a measure of the extent of reaction and any kinetic deductions from rates of pressure change are very suspect.

1.8 Surface Effects

A notorious feature of combustion reactions has been the difficulty in obtaining reproducible results, the cause being readily traced to surface effects. A new reaction vessel has to be 'conditioned' by carrying out several oxidations before kinetic parameters become constant. Even after this, experimental procedure, regarding pumping out time etc., has to be rigorously standardised to maintain consistent results. Mulcahy and Ridge[95], using a strict routine in the oxidation of propylene, were able to reproduce induction periods to within 1%. On the other hand, Bell and Tipper[86b] could not obtain consistent reaction rates at all in the oxidation of methyl alcohol in a glass packed vessel at 440°.

Deviation from normal running procedure by, for example, cooling the reaction vessel, pumping out for excessive periods, or admitting air or oxygen without fuel, upsets the equilibrium condition of the vessel and the surface has to be brought back to standard condition by another series of 'running-in' oxidations. Upsets of this type in standard procedure normally result in a shortening of the induction period and increase in maximum rate, although McEwan and Tipper[96], studying the oxidation of cyclopropane, found that when the reaction vessel was exposed to hydrogen a subsequent oxidation exhibited a lower rate.

The cause of surface effects has been supposed by Combe and Niclause[97] to be due to traces of polymer collecting on the surface but Szabo[98] considered the ageing process to be due to the surface being cleaned.

Norrish and Reagh[99], using reaction vessels of different diameters over an eighteen fold range, found that if the diameter were sufficiently reduced, the reaction rates of oxidations of a series of saturated and unsaturated hydrocarbons dropped abruptly towards zero while the corresponding induction periods increased towards infinity. This demonstrated that in narrow vessels, surface deactivation could predominate over other processes of deactivation. McEwan and Tipper[96] found that the maximum rate and length of inducation period in the cyclopropane oxidation varied by a factor of two over a series of vessels all of approximately the same dimensions.

Surface effects have been studied by carrying out reactions in vessels coated with various inorganic compounds such as boric acid, potassium chloride, lead oxide, sodium hydroxide, silver or silicic acid (as a result of washing the reaction vessel with a solution of hydrogen fluoride).[96, 100, 101, 102].

Variations in surface effects have been attributed to the activity of the surface towards hydrogen peroxide decomposition[103, 72]. For example acid coated surfaces preserve the peroxide, while salt, basic

and metallic surfaces destroy it. This will be dealt with more fully in a later section. The effect of surface has been considered essentially as affecting the kinetics of the reaction by participating in initiation, termination, and branching processes, whereas the propagating steps, which are almost completely responsible for product build up, have been accepted as being entirely homogeneous.

Satterfield and Reid,[104] however, studied the oxidation of propane in a flow system on a variety of surfaces under the same conditions of temperature, propane/oxygen ratio, and percentage oxygen consumption and found that the product distribution varied considerably, especially with minor products. They concluded that propylene and methyl alcohol were formed by homogeneous processes whereas the formation of ethylene was heterogeneous. The production of acetaldehyde and hydrogen peroxide increased substantially with decreasing surface activity.

The effect of surface on the oxidations of methane and formaldehyde has been studied by several Russian workers. In formaldehyde oxidation at temperatures above 500°, Anisonyan, Beider, Markevitch, and Nalbandyan[105] found that the oxidation rate was greatly reduced by packing the reaction vessel with glass tubes, or coating the surface with potassium tetraborate. This was confirmed by Markevitch and Fillipova[106] who studied the same oxidation between

330° and 550°. They found that, in a potassium borate coated vessel, about 70% of the heat of reaction was liberated close to the walls of the reaction vessel. The activation energy of the reaction in the same vessel was 50k.cal.mole^{-1}, compared with a range of values quoted in the literature, for the same reaction in uncoated vessels, of 18-29k.cal.mole.$^{-1}$

Enikolopyan and Bel'govskii[107], using a silver coated vessel, found that the oxidation of methyl alcohol was completely heterogeneous and proceeded through the initial production of formaldehyde which was desorbed into the gas phase but homogeneous oxidation of the resulting aldehyde and excess methyl alcohol was suppressed by rapid destruction of active centres at the silver surface.

The foregoing evidence suggests that a larger proportion of the reaction than has previously been supposed may well occur by heterogeneous processes on the walls of the reaction vessel.

1. 9. Modern Hydrocarbon Oxidation.

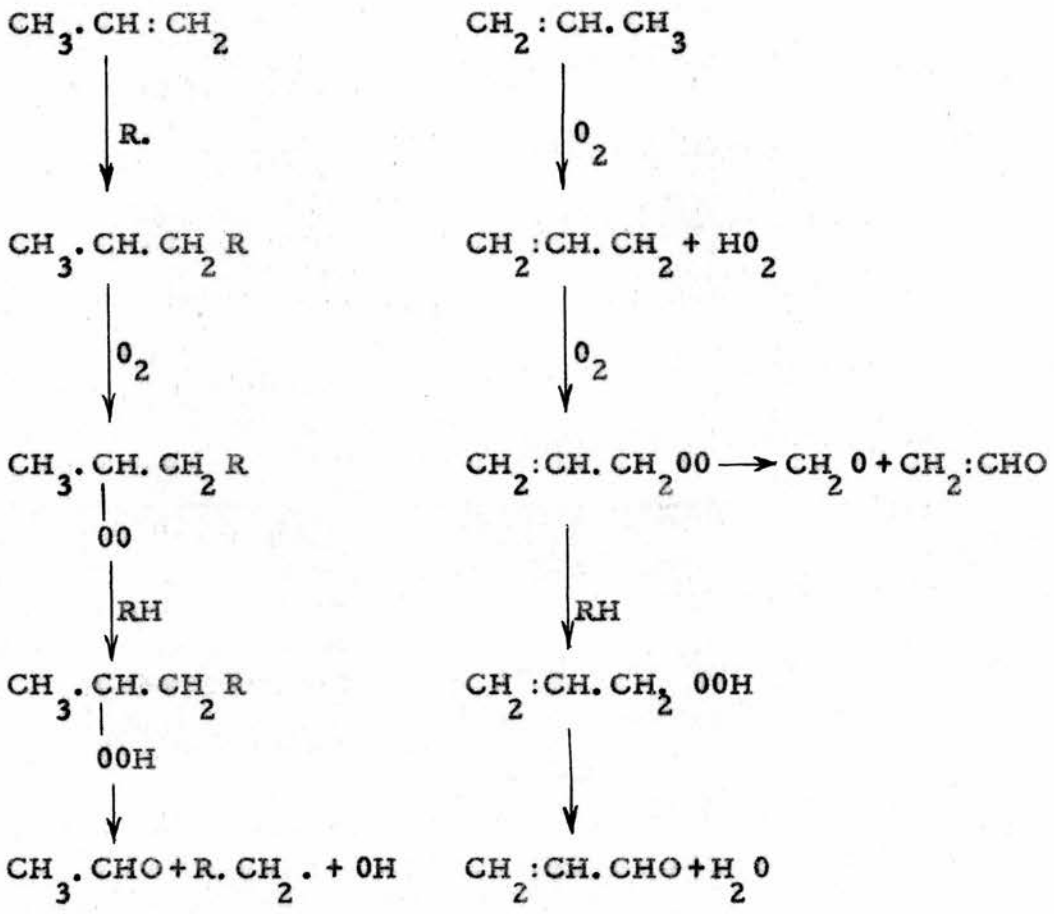
Mullen and Skirrow[108] examined the oxidation of propylene in a static system at temperatures from 300° - 400°, and hydrocarbon to oxygen ratios from 10:7 to 5:14. Under all conditions, the amount of total aldehyde was greater than formaldehyde. Since the total aldehyde contained ca. 10% acrolein, and under the experimental conditions employed, acetaldehyde would probably oxidise faster than formaldehyde, the ratio of acetaldehyde: formaldehyde in the system propylene: oxygen = 5:7, (calculated from the published results), could not have been less than 10:1 at the end of the induction period, falling to about 3:1 as the oxidation progressed. The significance of this will be discussed later.

This oxidation was unique in that the maximum rate of pressure change occurring during the reaction gave an accurate measure of the rate of oxidation. The reaction rate approached oxygen independence only under conditions of excess propylene. Excess hydrocarbon reduced the reaction rate and extent of reaction. This property was a feature of subsequent oxidation studies.[91] It was suggested that suppression of the oxidation by excess olefin was due to the formation of resonance stabllised allyl radicals formed by hydrogen abstraction.

$$CH_3.CH{:}CH_2 + O_2 = CH_2 \cdots CH \cdots CH_2 + HO_2$$

The oxidation products were thought to arise from hydroperoxides which were formed after initial hydrogen abstraction, (cf. Walsh[109]), and

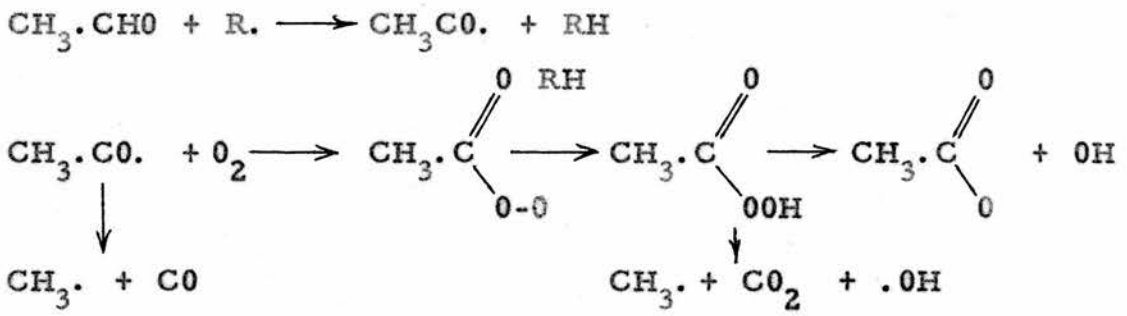
radical addition to the double bond.



That addition to the double bond and hydrogen abstraction occurred concurrently was shown by McNesby and Gordon[110] who photolysed deuteroacetone in the presence of four isomeric butenes and showed that addition of CD_3 radicals to either carbon atom of the double bond, as well as hydrogen abstraction from carbon atoms α to the double bond, occurred.

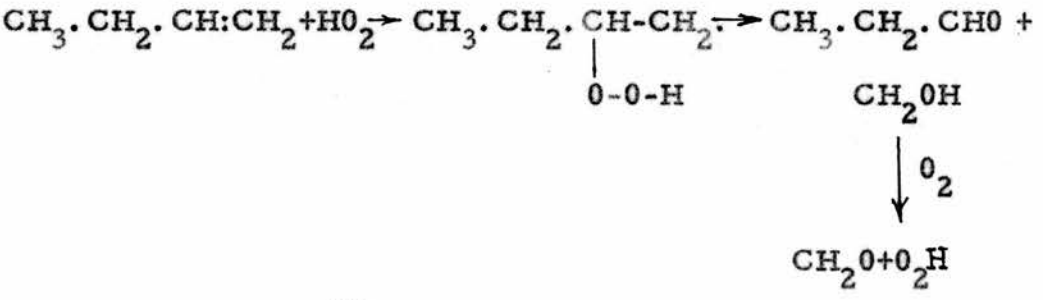
In the propylene oxidation, acetaldehyde was cited as the agent of degenerate branching although if reaction (a) above were the main

propagating step, it, too, would be the cause of branching.



The oxidations of but-2-ene[91] and hex-1-ene[92] were explained by the same type of mechanism[111]. A significant feature of the oxidations of propylene and hex-1-ene was the low quantities of formaldehyde compared to other aldehydes.

Badin[112] studied the oxidation of but-1-ene and but-2-ene at 20° in the presence of hydrogen atoms and found formaldehyde and propionaldehyde as major products from but-1-ene and acetaldehyde from but-2-ene. Since oxygen molecules and hydrogen atoms furnish HO_2 radicals[113], the oxidation could be represented[114].



Harding and Norrish[90] proposed a radical addition mechanism involving 0H radicals for the oxidation of ethylene and Norrish and Porter[115] later applied the same mechanism to the oxidation of n-butenes.

$$\begin{cases} C_2H_4 + 0H = CH_3. + CH_20 \\ CH_3. + 0_2 = CH_20 + .0H \end{cases}$$

$$\begin{cases} CH_3.CH{:}CH.CH_3 + 0H = CH_3.CH0 + C_2H_5 \\ C_2H_5 + 0_2 = CH_3.CH0 + 0H \end{cases}$$

This scheme is plausible enough for ethylene and but-1-ene oxidations where the methyl radical involved could only be oxidised to formaldehyde. It does not seem feasible when applied to olefins producing a larger alkyl radical however, e.g. but-2-ene, since the fate of an ethyl radical would almost certainly be oxidation to ethylene,[81, 116] a fact which was not observed experimentally[91, 115].

Skirrow and Williams[94] modified Norrish's mechanism to cover the oxidation of isobutene, which will be dealt with in the next section.

Cullis, Fish and Turner[93], on oxidising 2 methyl but-2-ene, explained the formation of equimolar quantities of acetaldehyde and acetone by the formation and subsequent symmetrical breakdown of a four membered ring peroxide.

$$(CH_3)_2.C{:}CH.CH_3 + 0_2 \longrightarrow (CH_3)_2.\underset{\underset{0\text{-}0}{|\ \ |}}{C\text{-}CH}.CH_3 \longrightarrow (CH_3)_2.CO + CH_3.CH0$$

This mechanism had the advantage of explaining the production of equivalent quantities of the two major oxygenated products, and also the initial pressure decrease, but a molecular reaction of this type, accounting for at least 80%

of the initial reaction, is not in keeping with the autocatalytic free radical nature of hydrocarbon oxidations generally accepted. Knox[85,117] has also pointed out that, in the oxidations of propane and ethane, the oxidation of propylene and ethylene, the major initial products, is governed by the same forces controlling the alkane oxidation which has been accepted as a free radical process.

The formation of a similar four membered ring peroxide had been previously suggested by Dobrinskaya and Neiman[118] as a possible route to acetaldehyde in the oxidation of but-2-ene. The formation of peroxides of this type, however, are not generally considered except as possible initiation steps[91, 115].

Minor products of the oxidation of 2-methyl but-2-ene were envisaged as arising from the three peroxy radicals:

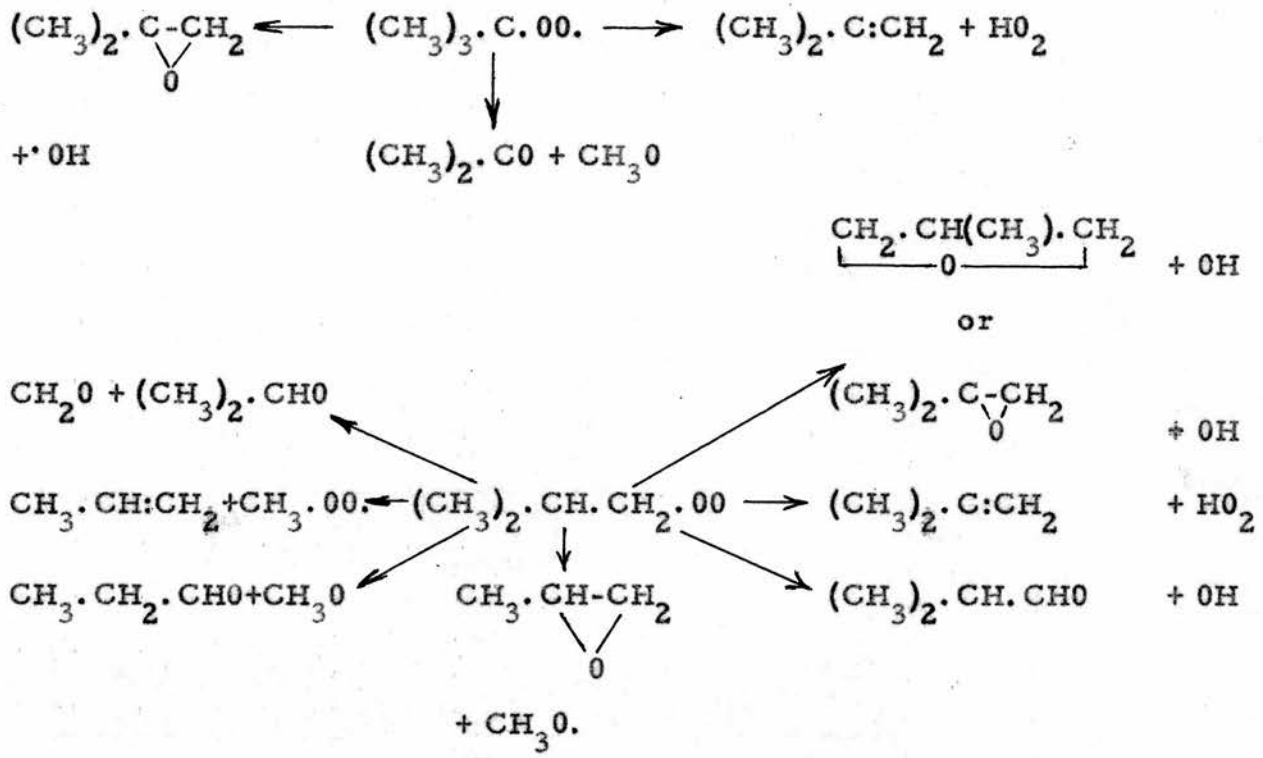
a) $Me_2.C{:}C(CH_3).00-$

b) $Me_2.C\text{-}CH(CH_3).00-$

c) $Me_2.\underset{\underset{00}{|}}{C}\text{-}CH(CH_3)$

If such a scheme applied to isobutene, the formation of a radical analogous to a) would require the initial abstraction of a vinyl hydrogen atom. Although no value is available for the strength of this bond, $D\boxed{CH{:}CH\text{-}H} = 104$k. cal., whereas $D\boxed{CH_2{:}C(CH_3).CH_2 - H} = 76$k. cal., so that such an abstraction would be unlikely to occur to any great extent. Also, there is no evidence in thermal gas phase oxidations below 500° of diradicals of types b) and c).

Bickel and Zeelenberg[116] studied the oxidation of isobutane at 300° and explained the formation of all the products of the reaction by homogeneous breakdown of initially formed t-butyl and sec-butyl peroxy radicals.



They found that variation of total pressure, temperature, or reactant composition had little effect on the distribution of products, with the exception of acetaldehyde and propionaldehyde.

Knox and Wells[82] postulated the formation of formaldehyde and ethylene, in the oxidation of ethane, by the reaction of ethyl radicals with oxygen, by

a) hydrogen abstraction, producing ethylene (80%),

b) formation of ethyl peroxy radicals which in turn yielded formaldehyde (5%) by homogeneous reactions.

A disturbing feature of the results was that the apparent activation energy difference between reactions a) and b) was 21k. cal. mole^{-1}. and an A factor ratio of 10^8, both values being high for reactions involving the same reacting species.

Similarly, Satterfield and Reid[78], studying the oxidation of propane, calculated the activation energy difference between the reaction producing propylene and that producing oxygenated products, as approximately 19k. cal. mole^{-1} and the A factor ratio 10^6.

1.10 Previous Work on Isobutene Oxidation

The only examination of the uncatalysed oxidation of isobutene of note has been carried out by Skirrow and Williams,[94] publication of whose work appeared during the course of the present investigation of the same olefin. The results, based on detailed product analysis, mainly by gas chromatography, gave a general picture of the reaction but left many facets of the oxidation unexplored.

The oxidation conformed to the general pattern of higher olefin oxidations, with hydrogen abstraction reactions from methyl groups occurring incidental to the main process of radical addition to the double bond. The reaction was studied at 250° and 320°. The importance of surface effects on the kinetics of the reaction was noted since two identical reaction vessels under the same conditions gave different oxidation rates, and different quantities of peroxide. A fuller investigation of surface effects was not attempted.

Pressure/time curves, which were not representative of the extent of reaction, showed the characteristics noted in other olefin-oxygen systems[92, 90, 91]. An initial pressure decrease was followed by an increase to the maximum rate and deceleration to constant pressure. The magnitude of the kinetic parameters was greatly influenced by the reaction conditions. The maximum rate of pressure decrease was independent of initial oxygen pressure but bore an

approximately third order dependence on initial isobutene pressure. The maximum rate of pressure increase passed through a maximum as the initial pressure of fuel was increased and increased steadily with increasing oxygen pressure.

At 320° the products were carbon monoxide, carbon dioxide, propylene, water, acetone, formaldehyde, acetaldehyde, isobutyraldehyde, methacrolein, propylene oxide, methane and acid. A significant feature of the oxidation was the absence of isobutene oxide at 320°, and only trace presence at 252°. One reaction vessel gave no peroxides but another identical reaction vessel gave small amounts of hydrogen peroxide and methyl allyl hydroperoxide, these products being identified by paper chromatography.

Acetone and formaldehyde accumulated in a roughly 1:1 ratio in the early stages and were the earliest detectable products. This was in contrast to earlier work, on propylene[108] and hex-1-ene[92], where the ratio of formaldehyde to the other major carbonyl product of the respective reactions was much less than 1:1.

The other major oxygenated products, isobutyraldehyde and methacrolein, accumulated steadily but were at all times less than either formaldehyde or acetone. The ratio of the yields of carbon monoxide to carbon dioxide was approximately five, and water, determined at the end of the reaction was shown to be a major product. Acetaldehyde yield was of the order of 5% of the methacrolein and at 320° hydrogen peroxide was barely detectable.

The addition of nitrogen had little effect except to slightly increase the maximum rate of pressure increase. Added acetaldehyde caused an increase in the maximum rate of pressure decrease and enhanced the total pressure decrease.

The initial pressure decrease could not be correlated to peroxide formation and, since under conditions of excess olefin the final pressure was less than the initial pressure, the products causing the pressure decrease must have been of a more stable nature than organic peroxides.

The production of equimolecular proportions of acetone and formaldehyde, each of which showed only slight autocatalytic development with time, could be explained by a radical chain addition mechanism involving hydroxyl radicals:

$$(CH_3)_2\cdot C : CH_2 + OH = (CH_3)_2\cdot \dot{C} - CH_2OH$$

$$(CH_3)_2\cdot \dot{C} - CH_2OH + O_2 = (CH_3)_2\cdot \underset{\displaystyle O - O}{\overset{\displaystyle |}{C}} - CH_2OH$$

$$(CH_3)_2\cdot \underset{\displaystyle O - O}{\overset{\displaystyle |}{C}} - CH_2OH = (CH_3)_2\cdot CO + CH_2O + OH$$

while an alternative route could explain the formation of isobutene oxide which, it was postulated, isomerised almost completely to isobutyraldehyde.

$$(CH_3)_2\cdot \underset{\displaystyle O - O}{\overset{\displaystyle |}{C}} - CH_2OH = (CH_3)_2\cdot \underset{\displaystyle O}{\overset{\displaystyle C - CH_2}{\diagdown\!\diagup}} + HO_2$$

With excess isobutene present, the possibility of addition of the peroxy radical to the double bond of a further fuel molecule was envisaged:

$$(CH_3)_2.\overset{\overset{O}{|}}{C} - CH_2OH + CH_2 : C.(CH_3)_2 \rightarrow (CH_3)_2.\overset{\overset{O-O}{|}}{C}-CH_2OH$$

$$O-O-CH_2.\dot{C}(CH_3)_2 \downarrow$$

$$(CH_3)_2.CO + (CH_3)_2.\underset{O}{C-CH_2}$$

$$+ CH_2OH$$

The resulting hydroxy methylene radical would then be oxidised to formaldehyde.

$$CH_2OH + O_2 \longrightarrow CH_2O + HO_2$$

Methacrolein was believed to be produced by hydrogen abstracted from a methyl group, followed by hydroperoxidation, and subsequent dehydration.

$$CH_2:C(CH_3)_2 \xrightarrow[-H]{} CH_2:C(CH_3)CH_2 \xrightarrow{O_2} CH_2:C(CH_3)CH_2OO$$

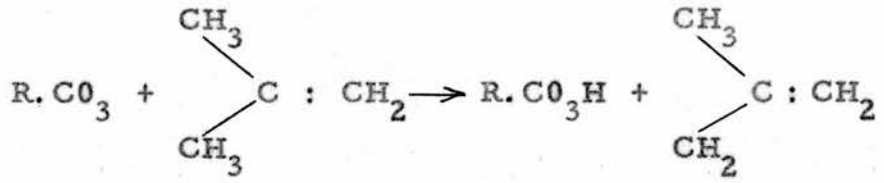
$$\downarrow RH$$

$$H_2O + CH_2:C(CH_3)CHO \longleftarrow CH_2:C(CH_3)CH_2OOH + R.$$

The aldehydes produced were considered to be the branching intermediates and the inhibitive effect of excess olefin attributed to the replacement of the peracid generating and propagating reaction.

$$R.CO_3 + R.CHO \rightarrow R.CO_3H + R.CO$$

by the reation:



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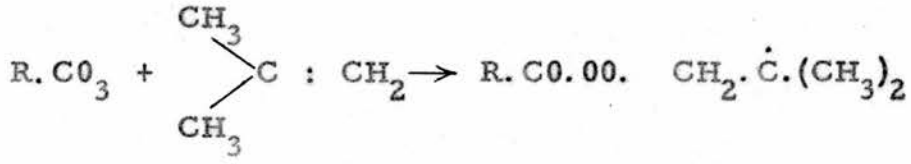


the products of this reaction being less effective chain carriers or branching agents than the corresponding products of aldehyde oxidation.

1.11 The present state of oxidation theories.

At the present time, there is no irrevocable proof of any mechanism which can be applied generally to hydrocarbon slow combustions. The various theories which have been proposed only suggest routes to products detected in the experimental work and do not differentiate between primary and secondary products. Seldom has any attempt been made to explain the kinetics of the reactions of higher hydrocarbons. For olefins, at any rate, the kinetics of the oxidations are rather obscure.

Nevertheless, several characteristic features of combustion reactions have evolved. Foregoing evidence has shown that hydroperoxy radicals exist in systems containing organic radicals and oxygen.

e.g. $C_nH_{2n+1} + O_2 = C_nH_{2n} + HO_2$

$C_nH_{2n+1}O + O_2 = C_nH_{2n}O + HO_2$

$CHO + O_2 = CO + HO_2$

and the initial stages of alkane oxidations have been accepted as :

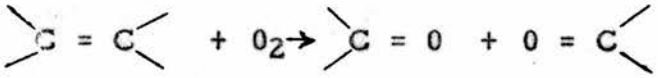
$$C_nH_{2n+2} + X = C_nH_{2n+1} + HX \qquad (1a)$$

$$C_nH_{2n+1} + O_2 = C_nH_{2n} + HO_2 \qquad (1b)$$

where X = a radical which can attack the alkane.

Although the fate of the HO_2 radical produced in reaction (1b) is uncertain, (and Knox and Wells[82] have argued that since it is rather unreactive it is likely to disproportionate when its concentration is high), under conditions of small percentage reaction and low reaction rate, it is most likely that X in equation (1a) can be identified with HO_2.

The position as regards olefin oxidation is still far from clear. The initial production of two molecules of carbonyl products can be represented:



: but the exact method of production of the carbonyl compounds is still not clear. Nor is the mode of production of the many diverse minor products of the reaction.

It is agreed that due to the free radical nature of combustions, e.g. the existence of explosive limits, cool flames, negative temperature coefficients, autocatalysis, effects of catalysts, inhibitors etc., the main processes producing major initial products must be homogeneous gas reactions. It has been argued previously that the most probable species attacking the fuel is HO_2 and due to the endothermicity of its reactions the main process with olefins is most likely to be addition to the double bond.

It is formally possible to derive most, but not all, of the products from the appropriate peroxy radicals by reasonable transition states. Cullis, Fish and Turner[93] in the oxidation of 2-methyl but-2-ene labelled with ^{14}C, at atoms 2 and 4, showed that all the products with the exception of t-butyl alcohol were formed without rearrangement of the carbon skeleton.

If any of the homogeneous schemes involving intermediate peroxy radicals outlined in section 1.9., could be applied to combustion systems in general and account for the formation of all the products, then the following should be true:

(a) the initial yields of products should be independent of oxygen and hydrocarbon pressure,

(b) the yield of each product should show slow unidirectional trends with temperature according to the Arrhenius equation, i.e. differences in activation energy between reactions responsible for the production of products would be expected to be small, as should their A factor ratios,

(c) product yields should be relatively unaffected by changes of reaction vessel surface, (although kinetic parameters may be substantially altered),

(d) all products should be easily accounted for through reasonably simple transition states.

In most of the work carried out on combustion reactions, sufficient experimental evidence has not been provided to satisfactorily satisfy all these conditions.

1.12 Initial Product Analysis.

Analytical methods until the early nineteen fifties depended to a large extent upon titrative and colorimetric analysis which of necessity in most cases required relatively large quantities of products. In order to satisfy the analytical requirements, it was almost impossible to study the early stages of reaction with any great accuracy or detail.

With the advent of gas phase chromatography however, a new analytical medium was introduced whereby complex mixtures could be quantitatively analysed with a good degree of accuracy,[119,120] and which, with suitable detector refinement, could satisfactorily cope with quantities of product as low as 10^{-7} mole.

It was mainly due to this advance that the mechanism of the initial stages of the low temperature alkane oxidations were elucidated, and it was established that the first intermediate product of such an oxidation was the corresponding olefin, (although this had been suggested previously for alkane oxidations at temperatures above 400°).

Measurement of the relative yields of products in the early stages of oxidation allows several conclusions to be drawn about fundamental processes. For example, Knox and Wells calculated the initial rates of formation of products against pressure change by measuring the initial gradients of respective products in the product pressure/ ΔP graph. In this reaction, it was suspected that ethylene and formaldehyde were both formed by the reaction of ethyl radicals with oxygen.

$$C_2H_5 + O_2 = C_2H_5OO \xrightarrow{(1)} C_2H_4 + HO_2$$
$$C_2H_5OO \xrightarrow{(2)} CH_2O + CH_3O$$

Thus, by measuring the relative initial yields of ethylene and formaldehyde produced at different temperatures, and applying the Arrhenius equation,

$$k = A \exp(-E/RT)$$

to the reaction, the following relationship was obtained:

$$\text{Rate (1)} / \text{Rate (2)} = A_1/A_2 \exp(E_2-E_1)/RT \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By plotting log of the ratio of the initial yields against $1/T$ the difference in activation energies, and the ratio of the A factors for the two reactions were obtained.

Since alkane oxidations produced an olefin as the initial major product, this led to the situation in the early stages of oxidation of there existing a primary intermediate product much more reactive than the parent fuel. Examination of the reaction products at any subsequent stage of the reaction could not then give an unambiguous knowlege of where the later products originated. It was, therefore, desirable to examine the products at as early a stage as possible in the reaction and this has been done by the use of flame ionisation detectors, whereby the reaction can be studied under conditions of less than 1% hydrocarbon conversion. With olefins, however, this refinement is not necessary since, except in certain cases the olefin itself is the most reactive compound present in the early stages.

Under conditions of very low conversion, pressure changes and

reactant consumption are small and cannot be measured accurately. An alternative method of obtaining relative initial yields of products has been applied by Knox[82] to the oxidations of ethane and ethylene and is now in general use. The absolute yields of products, measured in terms of carbon content are plotted against the total carbon content of the products. The gradient of any such line at any stage in the reaction then gives the net fractional rate of production of that particular product in terms of its carbon content. The sum of the gradients for all lines must be unity.

This method distinguishes between primary and secondary stable oxidation products. With the former, the plot of carbon content/total carbon falls below the initial gradient as the reaction proceeds whereas, with the latter, the opposite is the case since the initial gradient of a secondary product should be zero.

1.13 Aim of the Research

As described earlier, the low temperature oxidation of an alkane produces the corresponding olefin with the same number of carbon atoms in about 80% yield in the initial stages. It was therefore desirable to study the very early stages of the paraffin oxidation, in conjunction with a separate study on the olefin oxidation under approximately the same conditions. This has been done in this laboratory and the work presented herein represents the study of the oxidation of isobutene, the isobutane oxidation having been carried out concurrently by Mr. J. M. C. Turner.

The main body of the examination was to establish the effect of reactant pressure variation, and temperature variation on the product distribution, especially in the early stages of reaction.

Oxygen to isobutene ratios and isobutene to oxygen ratios were tested over a four fold range. Oxidations using one to one ratios of isobutene to oxygen were examined over a temperature range from 246° - 352°, incorporating a comprehensive product analysis at eight different temperatures within this range. By this means it was hoped to determine activation energy differences between reactions producing some of the more important products.

Although pressure-time parameters are difficult to interpret in olefin oxidations, the variation of these with reactant composition and total pressure were measured mainly for comparison with the results obtained by Skirrow and Williams[94].

At a later stage in the investigation it was suspected that the nature of the surface of the reaction vessel played a major part in the oxidations and the effect of changing the surface over a range from acid-base was studied in order to assess the influence of the surface on the product distribution.

SECTION B

EXPERIMENTAL TECHNIQUE

B - EXPERIMENTAL TECHNIQUE

1. Apparatus

The apparatus was essentially a conventional high vacuum static system, constructed mainly of pyrex glass (Fig. B. 1). Two deviations from the traditional type of apparatus were:

(a) the use of metal valves instead of glass stopcocks,

and (b) inclusion of a multi-sampler whereby up to ten samples could be taken during the course of one run.

1.1 General Apparatus

(a) Metal Valves

Metal needle valves were used instead of greased glass stopcocks. The metal to glass seals were made with 'Araldite' adhesive (CIBA (A.R.L.) Ltd., Duxford, Cambridge).

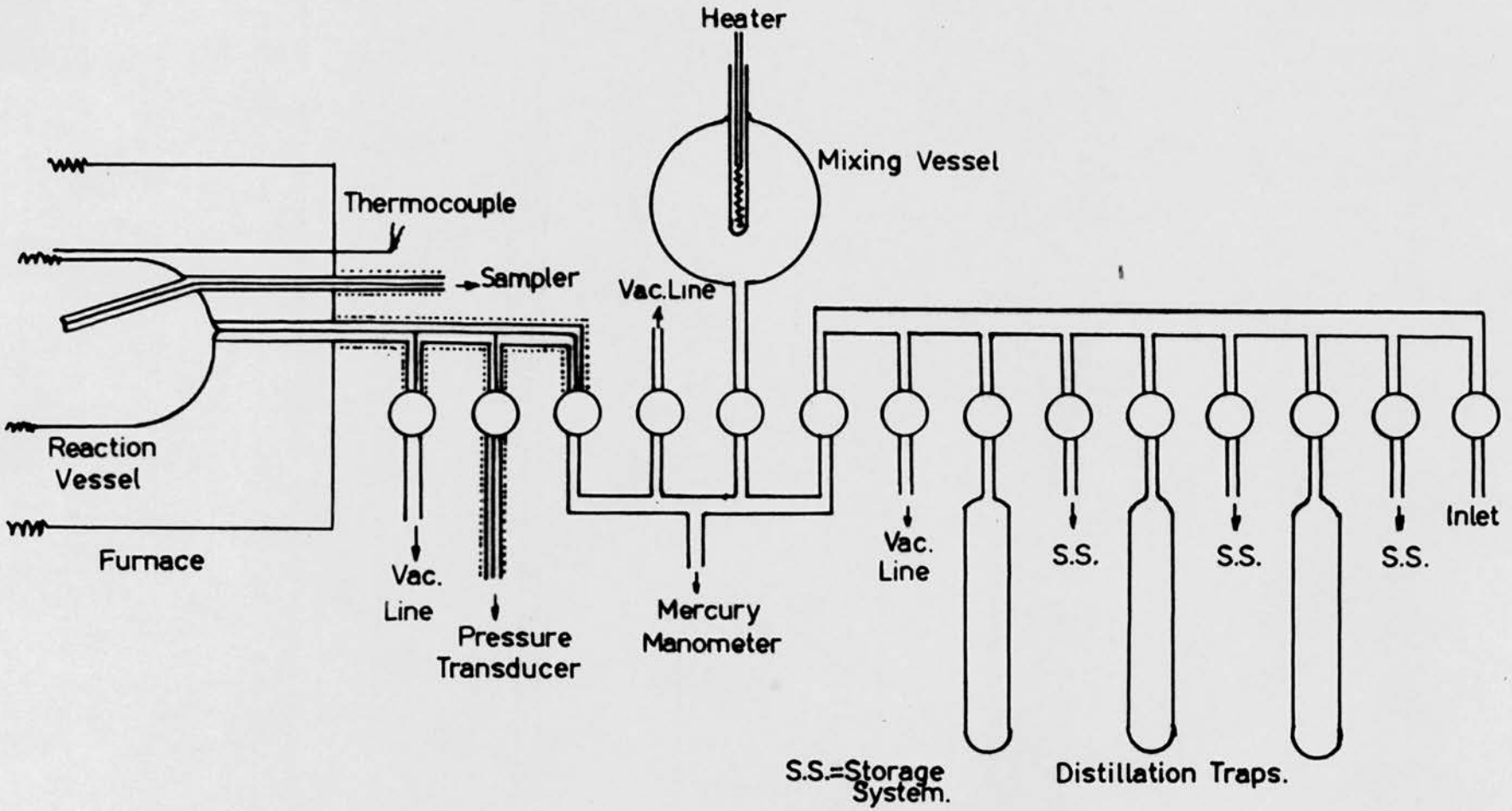
On the pre-reaction vessel side of the apparatus, 'Adams' valves (L. Adams Ltd., London N. W. 10), in which the vacuum tight gland was made of nylon were used. On the analytical side, stainless steel Hone valves (F. J. Hone & Co. London) which had a much smaller dead-space than the Adams valves were used, the pressure tight seal being made by 'teflon' washers.

(b) Pumping System

The pumping system consisted of a three stage mercury diffusion pump backed by a 'Speedivac' rotary oil pump (Edwards Ltd., Crawley, Sussex). With this system, the pressure in the apparatus could be

APPARATUS.

Figure B.1.



reduced to a 'sticking vacuum', measured on a vacuostat. This pressure corresponding to approximately 10^{-5} - 10^{-6} mm. Hg.

(c) Storage and Mixing

Purified reactants were stored in five-litre bulbs, fitted with 'cold fingers' for degassing purposes. Reaction mixtures were made up at room temperature in a one litre spherical vessel, which was afterwards heated by a 'hot finger' passing into the centre of the vessel, to ensure good mixing.

(d) Reaction Vessel

A cylindrical 'Pyrex' reaction vessel, with hemispherical ends, 5.5 cm diameter, volume 508 ml. was used. It had a 2 mm. capillary inlet at one end and a 0.5 mm. capillary outlet tube passing from the centre of the vessel to the sampler. The body of the reaction vessel was housed in a cylindrical aluminium jacket to promote uniform heating. The vessel was separated from the aluminium jacket and the jacket from the bottom of the furnace by asbestos cradle supports.

(e) Temperature Measurements

The temperature of the reaction vessel was measured by means of a thermocouple in conjunction with a Doran D. C. potentiometer. The thermocouple was constructed of T1/T2 thermocouple wire, (British Driver Harris Ltd.), which was supplied with a calibration chart. The thermocouple, encased in a glass sheath, passed between the reaction vessel wall and the aluminium jacket and could be moved along the length of the reaction vessel.

(f) Furnace

The furnace consisted of a silica tube, 66 cm. long by 9 cm. internal

diameter. It was heated by three independent windings of nichrome wire, of resistance 150, 100 and 150 ohms respectively, the whole being lagged and insulated by a mixture of glass and asbestos wool. The temperature along the reaction vessel was kept constant to within $\pm 1^{\circ}$ by using external variable resistors in conjunction with the furnace windings. The power was supplied by a 'Variac' transformer and the mean furnace temperature controlled by a Resistance Thermometer Controller, Type RT2 (Sunvic Controls Ltd.)

1.2. Kinetic Apparatus.

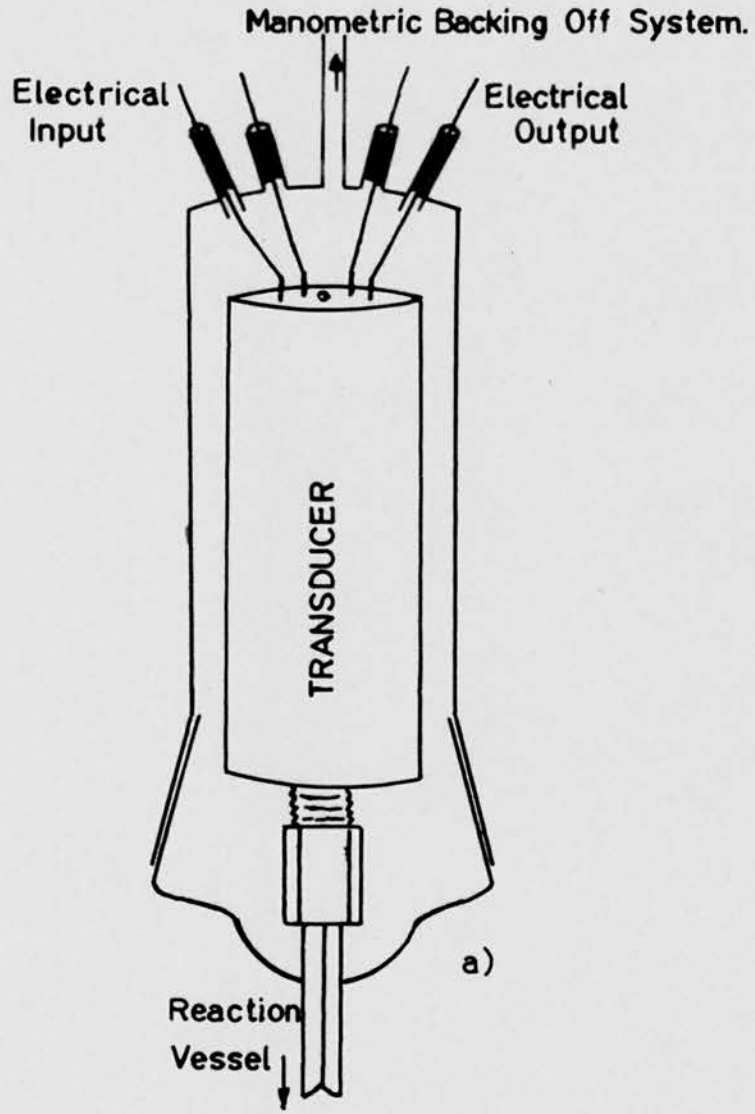
Pressure changes occurring during a reaction were measured by means of a pressure transducer (J. Langham, Thompson Ltd., Bushley Heath, England.) The input voltage was supplied by a battery of three two volt accumulators, the input being stepped down to five volts by means of a decade resistance box in series with the battery and transducer.

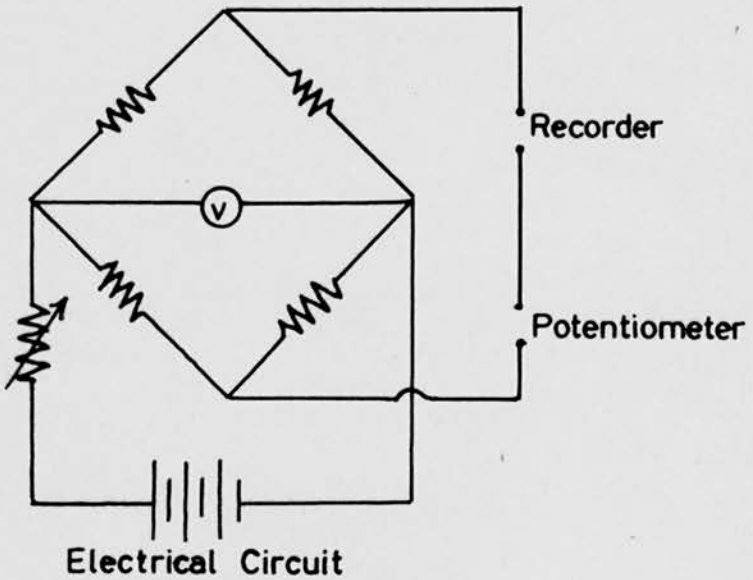
The gauge was encased in a glass container, (Fig.B.2a.), and the pressure in the reference side of the cell was adjusted with a mercury manometer. The output signal was recorded on a Honeywell-Brown Strip Chart Recorder. A Doran D.C. potentiometer, in series with the recorder supplied an electrical backing off voltage to keep the recorder pen on scale. (Fig.B.2b.)

A 15 mm. Hg. pressure change in the test chamber of the transducer provided a full scale deflection on the chart, (27.9 cm.).

PRESSURE TRANSDUCER SYSTEM.

Figure B.2.





The chart pen deflection was linear with pressure change over limits in excess of those used in this work.

The transducer was connected to the reaction vessel by 2 m.m.I.D. pyrex capillary, suitably heated by nichrome wire and lagged with asbestos rope to prevent product condensation in the gauge.

1.3. Analytical Apparatus.

(a) Sampling System (i)

The sampling system for all products except water, formaldehyde and hydrogen peroxide is shown in Fig.B.3a. It consisted of ten sample bulbs, each of approximately 2 ml. volume, with 0.5 mm. capillary necks so that virtually all the sample bulb could be immersed in a quart Dewar flask. The fine capillary manifold was wound with nichrome heating wire and lagged with asbestos to prevent product condensation.

The sampler was connected to a 'dip' line made of 0.5 m.m. capillary passing into the centre of the reaction vessel. The sampler was also fitted with leads to the Toepler pump, main vacuum line and injection system, all appropriate lines being heated to about 100° to prevent condensation.

Sampling System (ii)

The sampling system for formaldehyde and hydrogen peroxide analysis was similar to that above except that detachable bulbs were

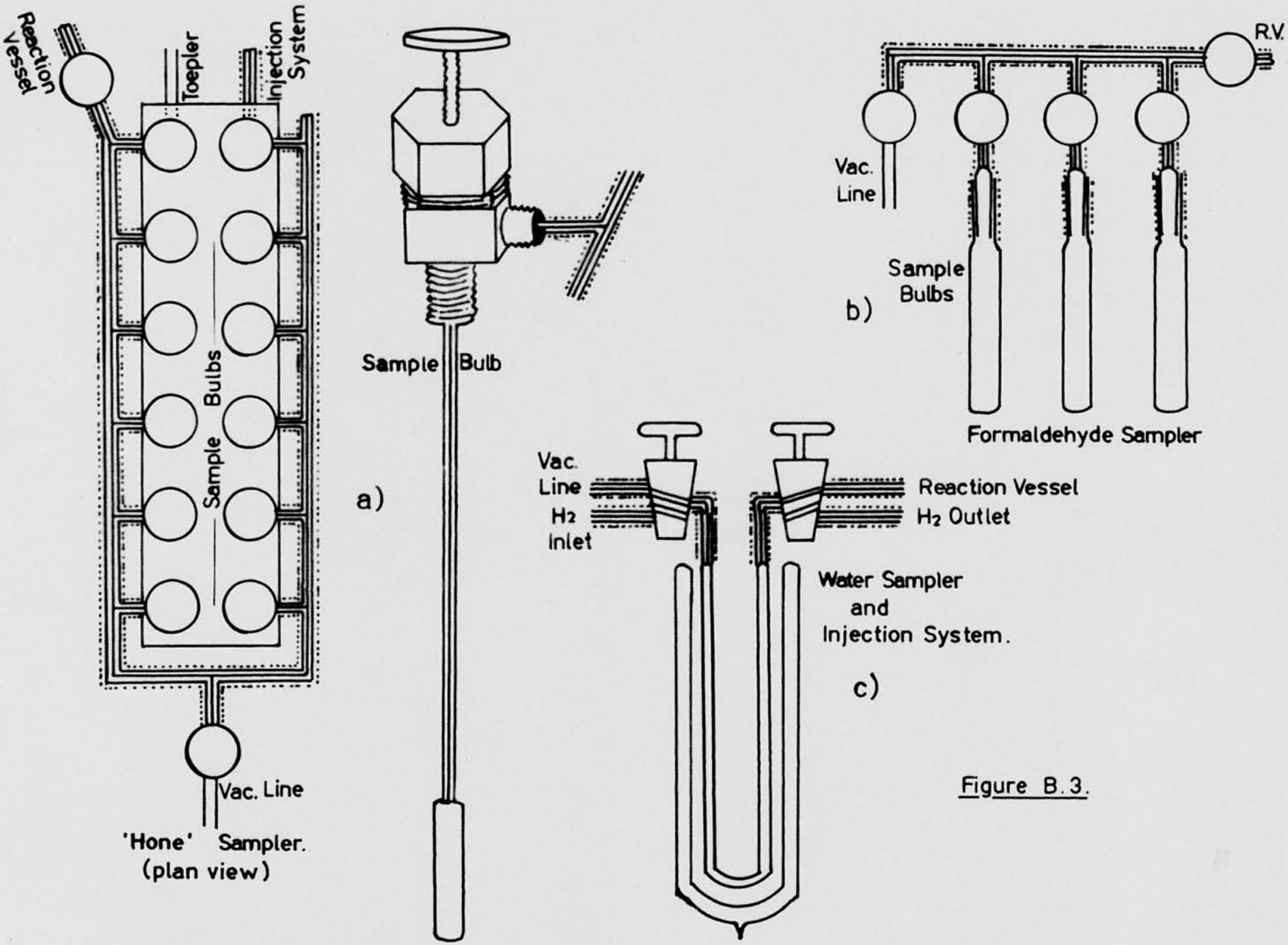

Reaction Vessel
Toepler
Injection System
Sample Bulbs
Vac. Line
'Hone' Sampler.
(plan view)
Sample Bulb
a)
R.V.
Vac. Line
Sample Bulbs
b)
Formaldehyde Sampler
Vac. Line
H2 Inlet
Reaction Vessel
H2 Outlet
Water Sampler and Injection System.
c)

Figure B.3.

employed (Fig.B.3b.). The capillary tops were heated and lagged to prevent condensation.

Sampling System (iii)

Samples for water analyses were taken into a glass 'U' tube fitted at each end with two way capillary stop cocks (Fig.B.3c.) This also served as an injector for water analyses, the whole system being maintained at 100°.

(b) Toepler Pump.

The Toepler pump contained three graduated volumes so that a wide range of sample pressures could be accommodated. The pump was fitted with a mercury filled glass non-return valve and was connected to the sampler and the injection system.

(c) Injection System.

The injection system comprised of a 'U' tube fitted into an assembly of five Hone valves which allowed:

(i) evacuation of the injection system,

(ii) entry from the sampler,

(iii) entry from the Toepler pump,

(iv) passage of the carrier gas.

The 'U' was constructed of 2-3 mm.I.D. pyrex tube. The other lines and connections were of 0.5 mm. capillary suitably heated and lagged to eliminate condensation.

(d) Carrier Gas.

Hydrogen was used as carrier gas. On leaving the cylinder the gas was passed through a set of stabilisers which consisted of alternate lengths of fine capillary and wide bore glass tube fused together. This had the effect of buffering the crudely regulated gas to an even flow. The gas was then finely regulated to the required flow rate by means of an Edwards reducing valve, and dried by passing through columns of calcium chloride and activated Linde Molecular Sieve.

The gas flow was then split; approximately half going to the injection system the rest being diverted through a 'dummy' column to one arm of the katharometer detector. After the injection system the carrier gas passed through the chromatography column and then to the other arm of the detector.

(e) Flow Rate Measurements.

Flow measurements were made by a soap film flowmeter attached to the exhaust from the katharometer.

(f) Chromatography Columns.

Four gas chromatography columns were used for the detection of reactants and most of the products. Details of the columns are given in Table B.1.

All the columns were made up from five feet, 'U' shaped pyrex glass tube, 3-4 m.m. internal diameter. The connections for columns longer than this being made by short 'U' shaped lengths of 0.5 mm. capillary, butt jointed to the column.

TABLE B.1.

Column Number	Length (feet)	Packing	Stationary Phase	Running Temp.	Flow Rate (ml/m.)	Compounds Analysed
1	3	Linde Mol. Sieve 13X (40-60)	-	20°	10	Oxygen Methane Carbon Monoxide
2	15	Firebrick (60-90)	Acetonyl Acetone (20%)	20°	25	Carbon dioxide Propylene
	5	Firebrick (60-90)	Dinonyl Phthalate (20%)			isoButene
3	15	Celite (60-80)	Polyethylene Glycol (8%)	20°	30	Acetaldehyde Propylene oxide isoButene oxide Propionaldehyde isoButyraldehyde Acetone Methacrolein
4*	7	Haloport 'F'	Carbowax20M (5%)	75°	30	Water

*Commercial column packing, supplied ready for use. (Fand M Scientific Corp., PA., U.S.A.)

(g) Detector

The detector was a thermal conductivity cell or katharometer. (Gow-Mac 9285D. Gow-Mac Instruments, New Jersey.) The cell was housed in a brass block approximately 2" square. Each arm of the gauge had a resistance of 20 ohms. The cell was well insulated with cotton and asbestos wool. The 'out of balance' current from the cell, produced when

a foreign substance eluted from the chromatography column, was fed to a Honeywell-Brown recorder which was suitably attenuated to cope with signals up to 187 mV. full scale deflection.

The power to the Wheatstone bridge circuit was supplied by four two volt accumulators. The bridge voltage was kept constant at six volts by means of a variable resistor in series with the battery.

A complete line diagram of the analytical apparatus with katharometer circuit, is shown in Figure B.4.

Line diagram of ANALYTICAL APPARATUS.

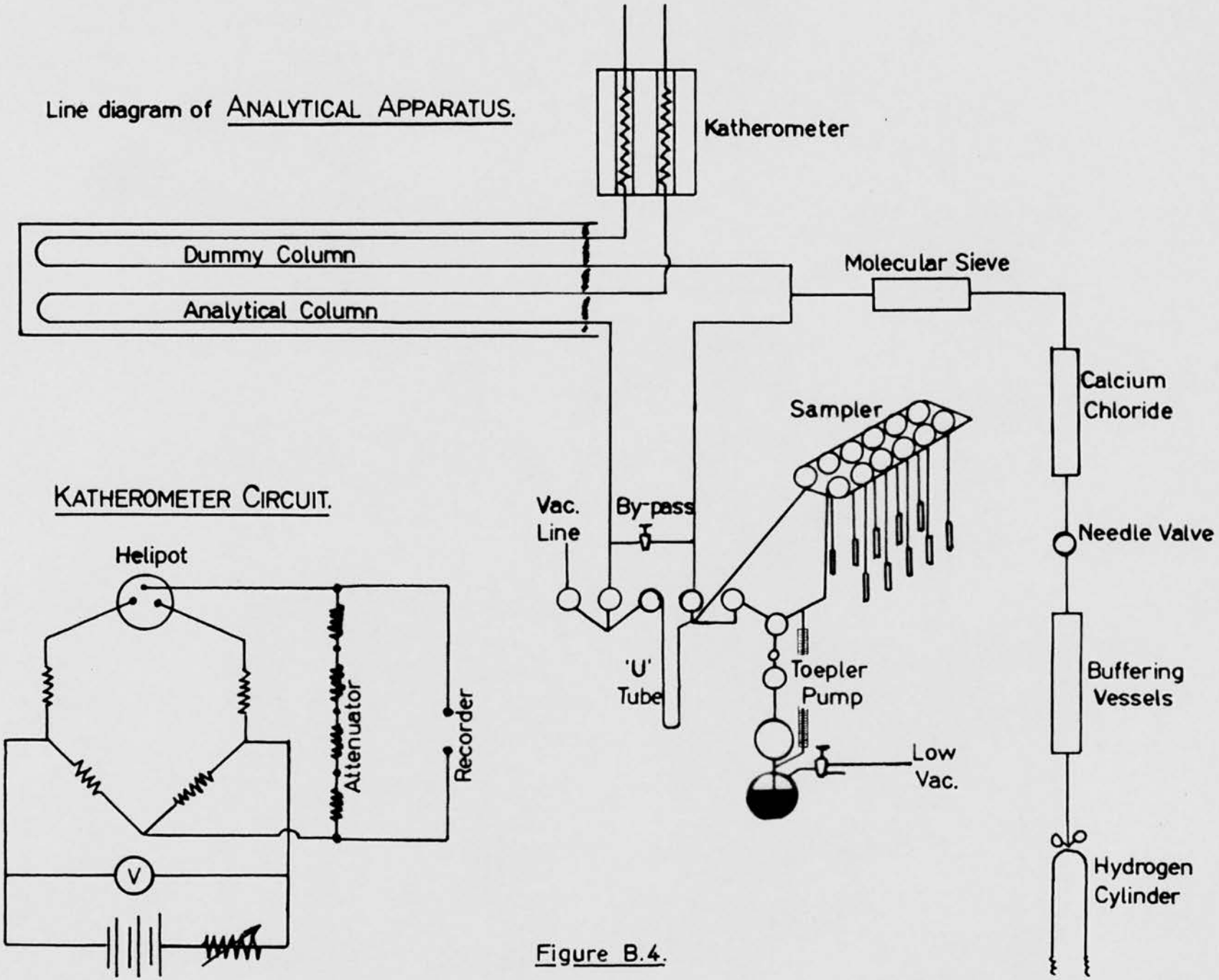


Figure B.4.

2. Preparation and Purification of Materials

2.1 Column Packings

(a) Partition Chromatography

Column 2: i) Acetonyl acetone, 20% by weight of the firebrick to be used, was dissolved in a suitable excess of acetone, and added with continuous stirring to the firebrick. The acetone was drawn off on a water pump, and the firebrick, impregnated with acetonyl acetone, was packed into three 5' lengths of 'U' shaped pyrex glass tube. ii) 20% by weight of dinonylphthalate was dissolved in a suitable volume of 40° - 60° petroleum ether. The solution was added with stirring to the firebrick, and the same procedure carried out as above. The firebrick coated with dinonylphthalate was packed into a five foot pyrex 'U' tube.

The four sections were joined together by 0.5 mm. capillary tubing. Since acetonyl acetone is volatile, the column was arranged so that the 5' of dinonylphthalate came immediately before the detector. In this way, any acetonyl acetone 'bleeding' off the first part of the column was trapped in the dinonylphthalate section and prevented from reaching the detector.

Column 3: Polyethylene glycol, 8% by weight of the celite to be used, was dissolved in acetone and added with continuous shaking to the celite. The acetone was evaporated by heating the slurry to 60° under water pump vacuum. The powdery packing was filled into four 5' 'U'

tubes of pyrex tubing, which were joined together by 0.5 mm. capillary tubing.

(b) Adsorption Chromatography

Column 1: Pellets of Linde Molecular Sieve Type 13 X were crushed and sieved. The 40-60 fraction was heated over a Meker burner for three hours. The powder was cooled in a vacuum desiccator and packed into a 3' pyrex glass column.

2.2 Reactants

isoButene: isoButene, (ex B.H.C. Co. Ltd., Grangemouth), contained 0.3% isobutane and 0.1% propylene plus n-butane as impurity. The gas was further purified by trap to trap distillation from 20° to -183° the middle fraction being retained in each case.

Oxygen: Oxygen was taken directly from a B.O.G. cylinder and any condensible material present was removed by passing the gas slowly through a liquid nitrogen trap. The gas was not purified further and normally contained 0.5% nitrogen.

2.3 Materials used for calibration, apart from reactants, were obtained as follows :-

Methane:	B.O.G. cylinder
Acetaldehyde:	B.D.H. Lab. Reagent.
Propylene Oxide:	B.D.H. Lab. Reagent.

Propionaldehyde:	B. D. H. Lab. Reagent.
isoButyraldehyde:	B. D. H. Lab. Reagent.
Acetone:	"Analar" B. D. H.
isoButylene Oxide:	Sample presented by I. C. I.
Methacrolein:	L. Light & Co. Ltd.
Carbon Dioxide:	Commercial "Drikold". Purified by distillation under vacuum, the middle fraction being retained.
Propylene:	Prepared by the action of P_2O_5 on iso-propyl alcohol. Purified by passage through successive traps at -80°. Further purified by trap to trap distillation, the middle fraction being retained in each case.

2.4 **Materials used in the preparation of columns :-**

Celite:	G. C. Ltd., G. Cel Plain, 60-80, 80-100.
Linde Molecular Sieve (13X)	B. D. H. Lab. Reagent.
Firebrick:	'Fosalsil' No. 6 Powder, Moler Products Ltd., Colchester.
Acetonyl Acetone:	B. D. H. Lab. Reagent.
Dinonylphthalate:	B. D. H. Lab. Reagent.
Polyethyleneglycol 400:	B. D. H. Lab. Reagent.

3. Reaction Vessel Coating

Since the condition of the reaction vessel surface is an important feature of oxidation reactions, a short history of the reaction vessel used will be given before the coating technique is described.

3.1 History of Reaction Vessel

The cylindrical pyrex reaction vessel had previously been used for many ethane and ethylene oxidations about 320°. Before commencing the present work, the reaction vessel was washed out thoroughly with concentrated nitric acid. It then had a sample outlet consisting of a 0.5 mm. capillary dipstick fused into the wall. The vessel was annealed overnight and fused on to the apparatus without further treatment. It was conditioned by carrying out many isobutene oxidations at 273° before the present series was started.

3.2 Boric Acid Coating

'Analar' boric acid was mixed with water to give a saturated solution at 50°. The solution was cooled to room temperature with stirring. (Solution A.)

Some more boric acid was dissolved by vigorous shaking in absolute ethyl alcohol to give a saturated solution at room temperature. (Solution B.)

The reaction vessel was cleaned by washing out several times with concentrated nitric acid and rinsing thoroughly with distilled water. It was then filled with a mixture of solutions A and B, (4:1), and allowed to stand overnight.

The solution was warmed to 30-35° and allowed to drain for one hour.

The reaction vessel was then fused to the apparatus, pumped out for three

hours at room temperature, and warmed to the required temperature under vacuum but without pumping. It was conditioned by carrying out three reactions, the last being left overnight.

3.3 Potassium Chloride Coating

Before coating the reaction vessel with potassium chloride, the residual boric acid was removed by shaking the reaction vessel for some time with ten separate volumes of boiling water.

The salt coating was applied by allowing the reaction vessel to stand full of 10% potassium chloride solution for half an hour. The solution was allowed to drain, the reaction vessel fused to the apparatus and conditioned as above.

3.4 Sodium Hydroxide Coating

The reaction vessel was coated exactly as above, using 10% sodium hydroxide instead of potassium chloride.

ERRATA

Page 73	last line	This	should read The .....
Page 75	P.3, l.1	The water	should read The volume of the water...
Page 97	last line	Section A	should read Section B.3.
Page 135	P.2, l.3	Figure C.36	should read Figure C.37.
Page 135	P.2, l.5	Figure C.36	should read Figure C.37.
Page 136	l.1	(figure C.36)	should read (figure C.37).
Page 192	P.4, l.2	The mean diffusion for	should read The mean diffusion time for .....
Page 202	P.2, l.5	the polymerisation	should read and polymerisation

4. Analytical Methods.

4. 1. Gas Chromatography

Gas chromatography was used for the analysis of oxygen, methane, carbon monoxide, carbon dioxide, propylene, isobutene, acetaldehyde, propylene oxide, isobutylene oxide, propionaldehyde, isobutyraldehyde, acetone, methacrolein, methanol and water. The columns used for the individual products are given in Table B.1. Samples to be analysed were introduced into the injection system and then passed through the appropriate column, to the katharometer. The amount of each substance present was correlated to the area of the peak produced from a previously constructed calibration graph.

4. 2. Other Methods.

(a) Formaldehyde Estimations

Formaldehyde was determined by a modification of the method of Bricker and Johnson.[121] The sample containing formaldehyde was shaken for a few minutes with chromotropic acid reagent (2 g. B.D.H. sodium salt for formaldehyde estimation, dissolved in a solution of 556ml. A.R. concentrated sulphuric acid and 320 ml. water). The solution was heated for half an hour in boiling water and left to cool to room temperature before being made up to the mark in a standard flask with more reagent. A known volume of this solution was then treated with thiourea solution which removed any red tinge. This absorption of the blue-violet solution

was compared to that of a blank determination using 10 mm. silica cells in an S.P.600 Spectrophotometer at a wavelength of 5700 A°. The concentration of formaldehyde present was then obtained from a previously constructed calibration graph.

Under the above conditions, none of the other products of the reaction interfered with the formaldehyde determination.

(b) Hydrogen Peroxide

Hydrogen peroxide was estimated by the method of Egerton et al.[122] To a portion of stock solution of 15% W/V titanous sulphate in sulphuric acid, dilute hydrogen peroxide was added until the solution was pale yellow. This solution was added to the sample suspected of containing hydrogen peroxide, and the absorption compared to that of a blank determination using 10 mm. silica cells in an S.P. 600 Spectrophotometer at 4100 A°. The concentration of hydrogen peroxide could then be determined from a previously constructed calibration graph.

5. Calibration of Apparatus.

5.1. Toepler Pump.

The calibrated volumes of the Toepler pump were measured by weighing the amount of mercury required to fill them. The total volumes were 0.47 ml., 4.13 ml. and 17.40 ml. from the respective graduation marks to the tap.

5.2. Injection System.

The injection system was calibrated by filling the 'U' tube with air at a known temperature and pressure. The air sample was then pumped into the Toepler where the temperature, pressure and volume of the sample were measured and the volume of the injection system calculated.

The water injection system was calculated by the same method.

5.3. Katharometer.

Starting materials and products to be analysed by gas chromatography were premixed with nitrogen or isobutene. A sample of the mixture was introduced to the injection system at a measured temperature and pressure. The sample was treated as under experimental conditions and passed through the appropriate column to the detector, under standard conditions of flow rate and detector voltage. The area of the resulting peak was measured by planimeter. This process was repeated for many samples at different pressures, from which a calibration graph of peak area/pressure in the injection system was compiled.

5.4. Pressure Transducer.

The circuit shown in Fig. 3b was used to calibrate the transducer. A small pressure was allowed into both chambers of the gauge so that ΔP across the transducer was zero. The recorder pen was adjusted to an arbitrary fixed position by altering the backing off e.m.f. The reference side was kept at this pressure, but the pressure in the test side of the gauge was increased stepwise. After each step the recorder pen was brought back to the same position by adjusting the potentiometer. A calibration curve was obtained by plotting P (mm.Hg.) against V (millivolts).

This procedure was repeated several times, giving a transducer constant of 15 mm.Hg./m.v.

5.5. Sampler (i)

The sample bulbs of the main sampler, (Fig.4a), were standarised against the volume of the injection 'U' tube using the pressure transducer.

The bulb to be calibrated was pumped out to a sticking vacuum and the valve closed. The reference side of the pressure transducer was kept at a constant pressure, and the test side and sampler manifold filled with an arbitrary pressure of air, near to an atmosphere (P1). This pressure was measured on a mercury manometer and the balance point of the transducer determined on a potentiometer. The sample was then allowed to share with the evacuated bulb. The change of voltage

required to obtain the new balance point, multiplied by the transducer constant (15.0 mm. Hg. /mV.) gave ΔP, and hence the new pressure in the system, (P_2), was obtained. These values were substituted in the equation:

$V_B = \left\{\frac{P_1}{P_2} - 1\right\} Vm+T$ where V_B = Volume of bulb to be determined

Vm+T = Volume of manifold + transducer

This equation contains two unknowns V_B and Vm+T, but repeating the above process with the injection 'U' tube, the volume of which had been previously determined by Toepler pump measurements, the constant Vm+T was evaluated, and hence the value of V_B calculated.

This procedure was repeated for each of the bulbs in turn.

The volumes of several of the bulbs were later checked independently by Toepler pump measurements. The results of the two methods were in excellent agreement.

Samplers (ii) and (iii)

The volumes of the water and formaldehyde samplers were determined by the Toepler pump method.

5.6 Integrator

The integrator (Perkin Elmer Corporation, Norwalk, Connecticut, U.S.A.) was used for measuring the areas of large peaks where the accuracy of the instrument was as good as that of a carefully planimetered peak area. The integrator was calibrated in two ways:

(i) By displacing the recorder pen sharply from the zero

count base line to some arbitrary distance up scale, and allowing to run in this position for a time. The pen was then returned to zero count base line as quickly as possible. Provided the pen displacements were done quickly and the time of displacement large, (normally 10 -15 minutes), the area integrated was essentially a rectange. The enclosed area was measured by drawing instruments and by planimeter.

This procedure was repeated several times for variable pen displacements.

(ii) By running samples of acetone through the system, and both integrating and planimetering the resultant peaks.

At various times during the course of the experimental work, spot ckecks of integrated peak areas were made by planimeter measurement.

5.7 Attenuator

The recorder was attenuated by placing a 'bank' of resistors in parallel with the katharometer output. The recorder input was then taken off any suitable step in the 'bank', (Fig. B.4). The total impedence of the attenuator was 1860 ohms. giving a series of attenuations from 1 - 187 m. V. full scale deflection.

The attenuator was calibrated in two ways:

(i) It was set up in a series circuit with a two volt accumulator and a decade resistance box giving a standard resistance of 1000 ohms. The potential drop across each step of the attenuator was then compared with that across the standard resistance, using a potentiometer.

The ratio of the resistors comprising the attenuator was thus obtained.

(ii) The attenuator was attached to the input of the recorder and a signal supplied by a potentiometer. The ratios of the steps of the attenuator were obtained by measuring the ratios of the e.m.f.s. required to give a constant pen displacement.

The results of the two calibration methods were in excellent agreement.

5.8 Calibration Limits.

Component	Measurement	Magnitude	No. of Measurements	Mean deviation	Standard diviation
Injection System:	Volume	2.99 ml.	10		0.3%
Toepler Pump:	Volume				
Volume 1		0.47 ml.	3	0	
Volume 1+2		4.13 ml.	3	0	
Volume 1+2+3		17.40 ml.	3	0	
Sampler:	Volume				
Bulb No.1		1.89	3	0.05%	
2		1.89	3	0.05%	
3		1.88	3	0.05%	
4		1.89	3	0.03%	
5		1.89	3	0.03%	
6		1.92	3	0.03%	
7		1.88	3	0.02%	
8		1.90	3	0.03%	
9		1.93	3	0.03%	
10		1.97	3	0.05%	
Integrator:	Counts/sq.in	1898	7		0.6%
Attennator:	m.V./full scale deflection	2.357	8		0.4%
		5.276	9		0.5%
		14.513	9		0.1%
		87.311	9		0.2%
Transducer:	Constant (mm Hg/mV)	15.0	75		0.9%
Katharometer:	Response (peak area/ pressure)				
	isobutene	11.34	72		1.8%
	acetone	56.21	28		0.8%

6. Experimental Procedure

6.1 Introduction

The analytical system involving a multi-sampler had the advantage that ten samples could be taken from the same run. Since the samples themselves were of the order of 1% of the total reaction mixture, the continuity of the run was not seriously disturbed. Several other disadvantages presented themselves, however. The analyses of formaldehyde and hydrogen peroxide, although this was discovered to be only a trace product, were not done gas chromatographically. The analyses of these products had to be divorced from the main set of oxidation runs since a detachable sampling system was required. It was found also that water could not be satisfactorily analysed using the metal valve system.

The analytical approach, therefore, was (a) to carry out the complete set of runs requiring gas chromatographic analysis, (b) repeat the oxidations with a new sampler for formaldehyde and hydrogen peroxide analyses, and (c) repeat the oxidations once again, with an all glass injection system, for water analyses.

The condition of the reaction vessel surface was critical to the rate of the reaction. For example, if oxygen was allowed into the reaction vessel some time before isobutene the reaction showed an enhanced rate. Similarly, if air leaked into the reaction vessel the

same situation arose, even if the air was pumped out for more than an hour. When the reaction vessel was disturbed in this way, it was found necessary to carry out at least two oxidations, the second one being allowed to continue overnight, to 'condition' the vessel and bring it back to its former state. To counteract possible leakage when the system was not in operation, the reaction vessel was normally filled with a pressure of the reactant mixture.

On account of the initial pressure decrease, pressure-time curves cannot normally be used to measure the extent of reaction in olefin oxidations. It was found, however, that occasionally two runs done under identical conditions went at slightly different rates. When this occurred, it was found that a good correlation between product concentration and pressure change was obtained by either of two methods :

(a) If the runs were slow, and the time lag between the two was of the order 10-15%, one pressure-time curve was projected on to the other at various points, where the differences between the two were conveniently measurable, and the values extrapolated back to zero time.

(b) In faster runs, the correction was made by finding the ratio of the reaction times, (i. e. the time taken to the point where $dP/dt = 0$, a point easily

observed on the pressure-time chart).

Due to the complexity of the analytical system and the lengthy preparation required for a run, occasional variations of rate between runs under the same conditions were corrected by one of the above methods, and an example of the 'projection' correction is given in Oxidation Number 8, (Section C.).

Due to the wide range of compounds encountered in the oxidation products, samples for gas chromatographic analysis had to be separated into three fractions,

(a) permanent gases which were toeplered off in liquid nitrogen,

(b) hydrocarbons and carbon dioxide, distilled from -80° to -190°,

(c) oxygenates, distilled from 60° to -190°.

Since some of the oxygenates were volatile at -80°, two separate runs had to be done to cover the complete range. This could be done in one of two ways; either,

(a) one run, comprising ten samples, for permanent gas and hydrocarbon analyses, and another run for analyses of oxygenates,

or (b) one run for analyses of permanent gases and oxygenates, and another run for analyses of hydrocarbons.

Normally the first of these was employed.

For oxidations going at fast rates, better correlation between the two runs was obtained by taking five 'double samples' (i. e. two sample bulbs filled simultaneously, at the same stage of the reaction), instead of ten single samples. This gave five analytical points for each of the products in the three fractions. The run was then repeated to obtain the normal ten analyses for each product.

6.2 Run Procedure

The system was pumped out under 'sticking vacuum' for one hour before the run commenced. The mixing vessel contained an excess of the mixture to be studied, and the temperature of the reaction vessel was checked at different points along its length. The sample bulbs were immersed in a quart Dewar flask containing water which had been maintained at room temperature for some time. The appropriate chromatographic column was set up under standard conditions of flow rate and detector voltage.

(a) Kinetic

The pressure transducer in conjunction with the potentiometer was connected to the recorder, and the backing off system adjusted to balance the reactant pressure and bring the chart pen to about mid-scale when the reactants were introduced to the reaction vessel.

The valve between the reaction vessel and the sampler was

left open for the first run. The first bulb of the sampler was left open, and the rest closed. The vacuum line valves to the sampler, and to the reaction vessel and transducer were closed and the mixture added to the reaction vessel at the desired pressure, and allowed thirty seconds to reach equilibrium. During this time the reactant pressure was read on a mercury manometer; the sample bulb valve, reaction vessel outlet valve and the reaction vessel inlet valve were closed. The sampler manifold was pumped out and bulb number two opened ready for the next sample. This procedure was continued until all the samples had been collected.

Since the first sample was taken at the same time as the reaction vessel was filled, no discontinuity was observed on the pressure time chart. Subsequent samples, however, were identified by a sharp drop in the pressure time curve. Samples were never normally taken at time intervals of less than two minutes, since manipulation of valves etc., and pumping out the sampler manifold took approximately this time. The temperature of the water bath was noted after every three samples.

An example of a ΔP/time plot, involving sampling five 'double samples', is given in Figure B.5.

(b) Analytical

The sample bulbs were immersed in liquid nitrogen for half an hour before their contents were analysed. The Toepler pump was evacuated, and the katharometer voltage and flow rate checked. The

KINETIC RUN. (The effect on total pressure due to multi-sampling.)

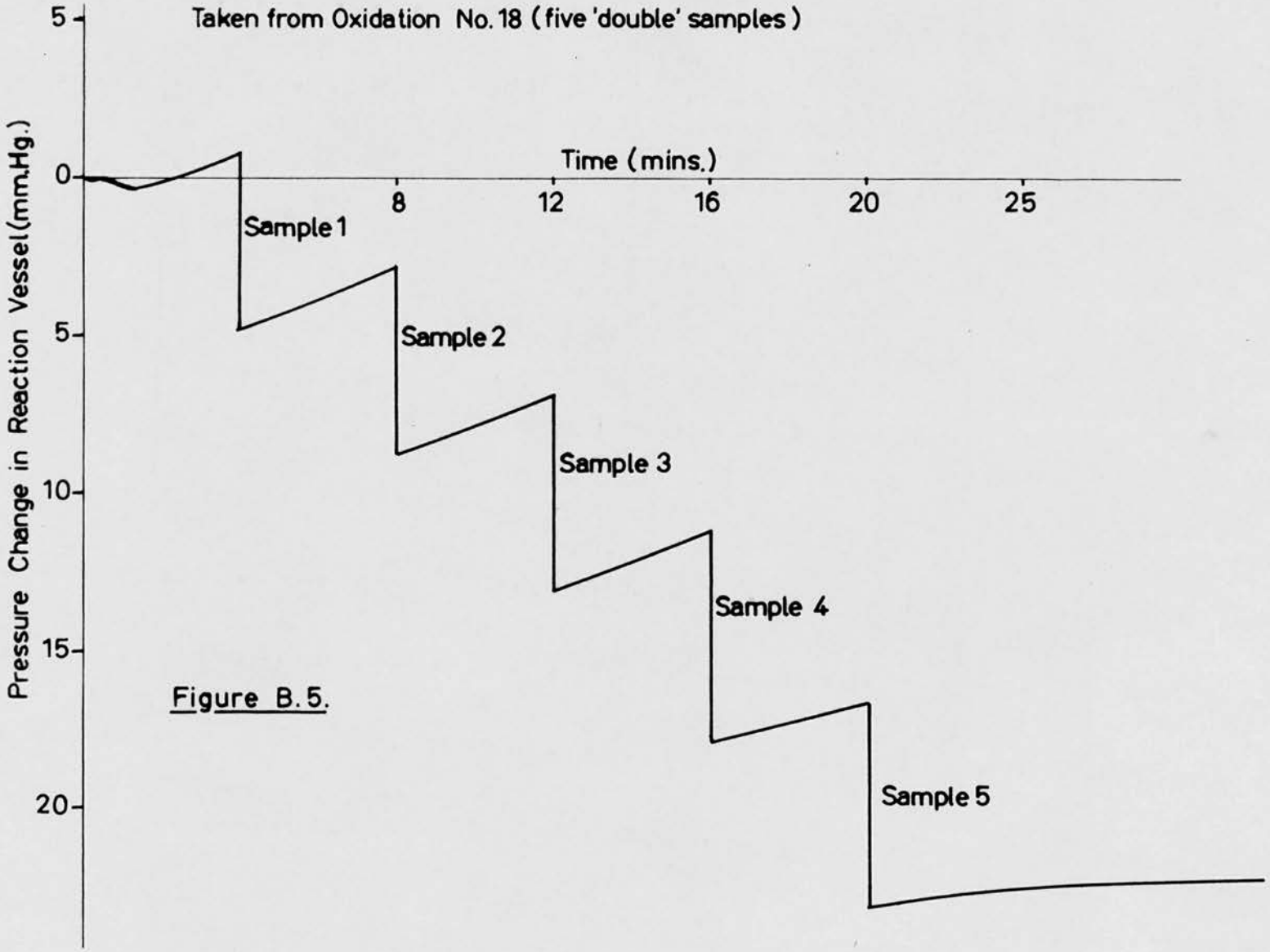


Figure B.5.

The electrical output from the katharometer was connected to the attenuator and the recorder.

Several blank injections were made into the column to ensure that no foreign substances were trapped in the lines of the analytical system.

6.3 Product Analysis.

(a) Permanent gases

Material from bulb number one, non-condensable in liquid nitrogen, was pumped into the calibrated volumes of the Toepler pump. The pressure, volume and temperature of the sample were noted and as much of the sample as possible pushed into the evacuated injector, and the connecting valve closed. Carrier gas was then flushed through the injection system for one minute and the sample passed through the Linde Sieve column at a flow rate of 10 ml. per minute. The residual gas in the connecting line between the Toepler and the injection system, was pumped back into the Toepler and its pressure, volume and temperature measured. From the two sets of measurements, the ratio of the number of micromoles of sample being analysed to the number of micromoles comprising the complete sample was obtained.

Permanent gases eluted from the column in the order oxygen, nitrogen, methane, carbon monoxide.

In preparation for the next sample the Toepler pump and injection system were pumped out during the course of the first analysis. This procedure was carried out successively until all the permanent gas analyses had been completed.

(b) Analysis of Hydrocarbons and Carbon Dioxide.

The sample bulbs were immersed in a solid carbon dioxide/acetone mixture at approximately -80° for half to one hour. During this time, column 1 had been replaced by the acetonyl acetone column, and this allowed to settle under standard conditions of flow rate, (25 ml./minute), and detector voltage. The same blank run procedure was carried out as previously to remove any extraneous material.

Each sample in turn was distilled into the injection 'U' tube, which was immersed in liquid nitrogen, for ten minutes. Vacuum was then applied through the 'U' tube to the sample bulb, for a few minutes. When the sample had been collected, the injection system was sealed off, and the sample flushed on to the chromatography column by passing carrier gas through the 'U' tube and at the same time replacing the liquid nitrogen trap by a flask of boiling water. The carrier gas was allowed to flow through the injection system for one minute.

Hydrocarbons and carbon dioxide were eluted from the acetonyl acetone column in the order carbon dioxide, propylene, isobutane (trace impurity in the isobutene), and isobutene.

(c) Analysis of Oxygenated Products.

A second run was done for oxygenates, using the same procedure as already mentioned above. If another set of permanent gas analyses were not required, the sample bulbs were immersed in liquid nitrogen and the excess permanent gases pumped off. This facilitated distillation of the oxygenated fraction which would not distil freely in the system when excess non-condensable gas was present.

Each sample in turn was distilled for 15-20 minutes from boiling water into the injection 'U' tube in liquid nitrogen. Vacuum was then applied as before to ensure that all the sample had been collected. The sample was injected as before, this time through the polyethylene glycol column, at a flow rate of 30 ml. per minute.

Oxygenated products were eluted in the order, acetaldehyde, propylene oxide, isobutene oxide, propionaldehyde, isobutyraldehyde, acetone, methacrolein, and methanol.

(d) Analysis of Formaldehyde.

The formaldehyde sampler was fused on to the reaction vessel outlet, and the vessel conditioned ready for analytical procedure.

Since the formaldehyde sampler was of larger total volume than the main G.C. sampler, only three sample bulbs were used. Formaldehyde analyses were correlated to the main body of products detected by G.C. by simultaneously analysing one of the products previously measured e.g. carbon monoxide or acetone.

Procedure.

The kinetic run was conducted as before and three samples taken in the detachable bulbs. The bulbs were then immersed in liquid nitrogen for half an hour, and carbon monoxide, if required, was toeplered off and analysed as before. If, however, an acetone analysis were required, formaldehyde could not be analysed in the same sample since the two could not be quantitatively fractionated.

After cooling, the bulbs were detached from the sampler, and while still immersed in liquid nitrogen, were filled with chromotropic acid reagent. The outside of each bulb was defrosted, dried, and deposited in a Ω. and Ω test tube, half filled with the reagent. The stopper was replaced and the lot shaken vigorously for five minutes to dissolve the formaldehyde.

The test tubes were placed in a boiling water bath, along with a blank sample, for half an hour, and the analysis carried out as previously described.

(e) Analysis of Hydrogen Peroxide.

Hydrogen peroxide was tested for by the same sampling technique. By this method however hydrogen peroxide was below the limits of detection. Further analyses for the peroxide were carried out by freezing out the complete reaction mixture in liquid nitrogen and continuing the analysis as previously described.

(f) Analysis of Water.

At selected times during the run, the two way stopcock between the evacuated 'U' tube and the reaction vessel was opened for ten seconds. The sample was flushed out of the 'U' tube to the chromatography column for half a minute. The 'U' tube was then pumped out, ready for the next sample.

The chromatography column, (number 4), was so designed, that water was adequately separated from other reaction products, but the whole analysis took only six-seven minutes. In this way, as many samples as the reaction time would allow, could be analysed and the sample kept gaseous at all times.

7. Calculation of results.

The kinetic graph obtained for pressure time changes with sampling, was of the type shown in Fig. B.5. Variations due to chemical reaction and sample removal were measured on the chart and converted to pressure units by multiplying by the transducer constant. Since removal of samples caused diminution in subsequent pressure variations, each pressure change had to be multiplied by the ratio:

$$\frac{\text{Pressure if no samples had been removed (theoretical pressure)}}{\text{actual pressure.}}$$

In this way each sample was characterised by a 'sampling factor' which had to be applied in any quantitative calculation. For a sample taken at the same time as the reaction vessel was filled, the sampling factor was unity.

Analysis of permanent gases.

The number of moles of permanent gas from the sample bulb, and the number left in the lines after injection was calculated as follows:

$$\text{Number of moles in Toepler} = \frac{P_T \times V_T \times 273}{760 \times 22{,}400 \times T_s} \quad \text{--------} \quad (1)$$

where P_T = pressure in Toepler pump

V_T = calibrated volume in Toepler pump

T_s = sampling temperature (^oK)

The pressure of any permanent gas in the sample bulb, and hence in the reaction vessel, since both come to equilibrium during sampling, was obtained from the expression:

$$Pmm = \frac{V_u \times A \times t_F^c \times T_s \times Att. \times f_1 \times f_2}{V_B \times C.F. \times t_F^o \times T_c \times Cal.Att.} \quad \text{------ (2)}$$

where Pmm = pressure of substance in the reaction vessel in mm.Hg.

V_u = volume of injection 'U' system

V_B = volume of sample bulb

A = peak area

C.F. = calibration factor (area/mm.pressure)

t_F^c = calibration time of unit gas flow

t_F^o = observed time of unit gas flow

T_s = sampling temperature (^oK)

T_c = calibration sampling temperature (^oK)

Att. = attenuation

Cal.Att. = calibration attenuation

f_1 = sampling factor

f_2 = ratio of total sample: quantity of sample analysed

which reduced to:

$$Pmm = \frac{A \times T_s \times f_1 \times f_2}{V_B \times t_F^o} \times K$$

where $K = \frac{V_u \times t_F^c \times Att}{Cal.Att. \times C.F. \times 293}$ and is a constant for any particular attenuation

Analysis of other products.

The pressures of hydrocarbons, oxygenates and water, were calculated from

the same equation. Since the complete sample was used for analysis, $f_2 = 1$.

Formaldehyde analysis

The kinetic run for formaldehyde analysis was carried out in the same way as described above. The pressure of formaldehyde in the reaction vessel at the time of sampling was given by:

$$Pmm = \frac{0.D. \times f_1 \times 7.6 \times 2.24 \times T_s}{V_B \times C.F. \times M_F \times 273} \quad \text{--------} \quad (3)$$

where 0.D. = optical density of sample

f_1 = sampling factor

V_B = volume of sample bulb

C.F. = calibration factor ($0.D./\mu g.CH_2O$)

M_F = molecular weight of formaldehyde

T_s = sampling temperature (^oK)

Worked Example

Application to oxidation No.19 (Section C)

isoButene : Oxygen = 1 : 1

Total Pressure = 214.5 mm.Hg.

Reaction Temperature = 303^o

Sampling Temperature = 20^o

Kinetic Run

Five 'double samples' were taken. Since the calculations involved are repetitive, only the sampling factors for the first two samples, and the pressure

of a few products in the first sample will be calculated.

Pressure-Time Chart

	mm. on chart	ΔP (mm.Hg.)
Start of reaction to Sample 1	- 3.5) +20.1) = +16.6	0.89
Decrease due to Sample 1	-104.9	- 5.65
Sample 1 to Sample 2	+ 36.0	+1.94
Decrease due to Sample 2	-110.0	- 5.92
and so on		

Initial Pressure = 214.5 mm.

	Start - Sample 1 and Sample 1	Sample 1 - Sample 2 and Sample 2
ΔP (mm.Hg.)	+ 0.89	+ 1.94
corrected ΔP	+ 0.89	+ 1.99
theoretical pressure	215.4	217.4
sample decrease	5.65	5.92
total decrease	5.65	3.98
actual pressure	209.7	205.8
sampling factor	1.027	1.057
ΔP in reaction vessel	+ 0.89	+ 2.88

From equation (1) :

Sample 1. No. of μ moles in sample bulb $= \frac{37.0 \times 4.13 \times 273}{760 \times 22{,}400 \times 292.0} = 8.39$

No. of μ moles left after injection $= \frac{65.0 \times 0.47 \times 273}{760 \times 22{,}400 \times 292.5} = 1.67$

$$f_2 = \frac{(\text{total sample})}{(\text{amount analysed})} = \frac{8.39}{6.72}$$

Product Analysis

Sample 1 was divided between bulbs 1 and 2. The portion of the sample in Bulb 1 was analysed for permanent gases and hydrocarbons, while the portion in Bulb 2 was analysed for oxygenates.

An example of one product analysis from each fraction is given below:

$$P_{\text{oxygen}} = \frac{2.99 \times 54.3 \times 1.000 \times 293.0 \times 1.027 \times 8.39 \times 87.311}{1.89 \times 87.311 \times 1.001 \times 1.396 \times 6.72 \times 293} = 79.2 \text{ mm}$$

$$P_{\text{isoButene}} = \frac{2.99 \times 32.0 \times 1.000 \times 293.0 \times 1.027 \times 87.311}{1.89 \times 87.311 \times 1.000 \times 1.133 \times 293.0} = 80.4 \text{ mm.}$$

$$P_{\text{acetone}} = \frac{2.99 \times 186.5 \times 1.000 \times 293.0 \times 1.027 \times 5.276}{1.89 \times 14.513 \times 1.010 \times 5.625 \times 293} = 19.2 \text{ mm.}$$

With values obtained from calculations of this kind, a product/time graph was constructed for the oxidation. Since both time of reaction and pressure change are unsatisfactory parameters in olefin oxidation, some other means of comparing successive oxidations had to be used. This will be described in Section D.

8. Elements Balance.

The maximum number of formaldehyde estimations per run was three and, due to the more diverse nature of the analytical method, formaldehyde analyses were normally confined to the early stages of the reaction. Elements balances are generally given up to the last formaldehyde estimation. Balances at later stages of the reaction were compiled using an estimated value of formaldehyde, based on its earlier development in relation to acetone.

The number of mm-atoms of C. H and O recovered did not vary by more than 5-8% from the amount initially used, and were often much closer than this. However, since isobutene was a major component of the sample mixture at every stage of the oxidation, the accuracy of the elements balance depended largely on the accuracy of its determination.

The elements balance indicated that no major product was unaccounted for.

SECTION C

EXPERIMENTAL RESULTS

Experimental Results

1. Introduction

The analytical and kinetic results obtained from the oxidation of isobutene are presented in this section along with results on the isomerisation of isobutene oxide.

Table C.O., (page 99), gives a summary of the experimental conditions under which each oxidation run was carried out. Each oxidation is numbered (from 1-23) and if any particular oxidation run is referred to in the text, reference to Table C.O. will supply details of the reaction conditions as well as the numbers of appropriate tables of results and figures pertaining to that oxidation.

Results of formaldehyde estimations, where they have been carried out, are given in the same table or table supplement as the gas chromatographic results, but, for convenience, graphs of formaldehyde runs have been grouped together in Figures C.24 - C.29, immediately after the main body of the results obtained by gas chromatography.

Note: In subsequent sections references to surfaces will be made as 'clean pyrex', or 'pyrex', 'aged boric acid' etc. 'Pyrex' or 'clean pyrex', refers to the non coated pyrex reaction vessel which was conditioned by carrying out many oxidation runs before this series began. The vessels coated with a layer of inorganic material were also conditioned before use as described in Section A. Three runs were then carried out

with each surface. The term 'fresh' refers to the first of the series of three, while 'aged' refers to the third of the series.

In the tables in this section, the following abbreviations have been used:

O_2	Oxygen
iC_4H_8	isoButene
C_3H_6	Propylene
Me_2CO	Acetone
iC_4H_8O	isoButene oxide
iC_3H_7CHO	isoButyraldehyde
C_3H_6O	Propylene oxide
MA.	Methacrolein
tr.	trace
-	not analysed

TABLE No. C.0.

Summary of Oxidation Conditions

OXID.n No.	Surface	iC_4H_8 :0_2	Total Pressure (mm. Hg.)	Temp.	Table and Fig. No.	HCH0 Table No.	HCH0 Fig. No.	H_20 Table No.	H_20 Fig. No.
1	Pyrex	1:1	200	273°	c. 1.	C. 1a	C24ab	C. 1a	C. 1.
2	"	1:2	318	273°	C. 2.	C. 2.	C25b.	C. 2.	-
3	"	2:1	150	273°	C. 3.	C. 3.	C25a.	C. 3.	C. 3.
4	"	1:2	150	273°	C. 4.	C. 4.	C25d.	C. 4.	C. 4.
5	"	2:1	300	273°	C. 5.	C. 5.	C25c.	C. 5.	c. 5.
6	"	1:1	200	273°	C. 6.	-	-	-	-
7	"	1:1	210	283°	C. 7.	-	-	-	-
8	"	1:1	206	293°	C. 8.	C. 8a	C26.	C. 8a	C. 8b
9	"	1:1	220	303°	C. 9.	C. 9a	C27ab	C. 9a	C. 9.
10	"	1:1	150	322°	C.10.	C.10a	C28b.	C.10a	C.10.
11	"	1:1	150	337°	C.11.	-	-	-	-
12	"	1:1	120	352°	C.12.	C.12a	C27cd	C.12a	C.12.
13	"	1:1	300	246°	C.13.	C.13a	C24cd	C.13a	C.13
14	Boric Acid	1:1	100	303°	C.14.	-	-	-	-
15	"	1:1	85	303°	C.15.	-	-	-	-
16	"	1:1	100	303°	C.16.	C.16.	C29a.	-	-
17	KC1.	1:1	215	303°	C.17.	-	-	-	-
18	"	1:1	215	303°	C.18.	-	-	-	-
19	"	1:1	215	303°	C.19.	C.19.	C29b.	-	-
20	NaOH	1:1	215	303°	C.20.	-	-	-	-
21	"	1:1	215	303°	C.21.	-	-	-	-
22	"	1:1	215	303°	C.22.	C.22.	C.29c.	-	-
23	"	1:1 $+N_2$	180 205	303°	C.23.	-	-	-	-

2. Analytical Results

2.1 The effect of varying reactant composition

Oxidations 1 - 5 were all carried out at 273°. In oxidations 1 - 3 the initial pressure of isobutene was maintained at 100 mm.Hg. while the pressure of oxygen was varied from 50 mm.Hg. to 200 mm.Hg. Similarly in Oxidations 1, 4 and 5 the initial pressure of oxygen was kept constant at 100 mm.Hg. while the pressure of isobutene was varied over the range 50 - 200 mm.Hg.

Oxidation No.6 represents the later stages of the oxidation of a 1 : 1 mixture at 273°.

TABLE No. C.1. (Figure C.1)

OXIDATION No.1

Ratio $iC_4H_8:O_2$ = 1 : 1 Total Pressure = 200 mm.Hg. Temperature = 273°

Pressure in Reaction Vessel (mm.Hg.)

Time (min.)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA.
0	0.00	105.7	98.3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	-	-	-	-	-	-	4.32	0.91	-	tr.	tr.	0.13
3	-0.22	91.6	92.9	1.33	0.12	0.09	-	-	-	-	-	-
5	-0.34	-	-	-	-	-	10.5	2.37	-	0.18	0.10	0.50
6	-0.33	83.8	83.9	3.59	0.44	0.19	-	-	-	-	-	-
9	-0.18	75.4	78.4	5.60	1.08	0.32	17.5	3.29	-	0.18	-	0.52
12	+0.01	71.6	77.3	8.75	1.71	0.39	18.4	3.69	0.00	0.36	0.12	-
15	0.27	66.6	74.4	10.9	1.33	0.42	20.0	4.27	0.00	-	0.13	0.58
18	0.53	64.0	72.3	12.8	2.40	0.45	21.9	4.12	tr.	0.45	0.17	0.63
21	0.97	-	71.5	14.5	2.92	0.52	23.1	4.68	0.11	-	0.17	0.66
24	1.33	48.7	67.9	16.7	3.28	0.59	24.2	4.88	0.20	0.37	0.18	0.79
30	1.91	48.1	64.2	20.0	3.29	0.54	26.6	4.72	0.22	0.44	0.20	0.91
40	2.88	-	-	-	-	-	28.5	5.26	0.51	0.48	0.24	-

Material Balance: mm. - atoms

Time	C	H	O
0	393	786	200
2	394	783	-
5	389	774	194
9	399	793	196
12	405	799	196
15	405	799	193
18	407	799	196
21	413	809	194
24	409	810	199
30	406	808	194

TABLE C.1.a (Figs. C.1, C.24a, b.)

OXIDATION No.1 Other Products

Time (min.)	HCHO (mm)	CO (mm)
1.25	1.19	
1.25	1.24	
2.50	2.34	
2.50	2.04	
2.50	2.89	
2.50	2.74	0.70
3.60	3.21	
3.60	3.53	
3.60	3.07	
3.60	3.37	
3.60	2.95	1.33
4.90	3.82	
4.90	4.34	
4.90	4.67	2.29
6.00	6.96	
6.00	5.00	
6.00	6.61	
6.00	6.06	
7.40	6.88	
7.40	6.33	
7.40	6.30	4.23
8.60	8.41	
8.60	8.06	5.25
9.80	7.95	
11.1	10.6	
11.1	10.3	8.16
12.4	11.7	
12.4	12.0	
12.4	10.3	
20.5	15.6	
26.5	18.6	
43.5	20.8	

Time (min)	H_2O (mm)
3.0	1.34
9.0	3.64
12.0	4.34
16.5	8.85
21.0	12.9
24.0	12.8
27.0	17.1
30.0	17.7
36.0	22.9
39.0	24.3
42.0	27.0
46.5	29.3
48.0	35.1
51.0	32.2
56.2	33.2
61.5	36.8
66.0	38.7
69.0	38.5
72.0	40.1
76.5	42.9
81.0	49.5
84.0	45.5
87.0	45.9
90.0	44.1

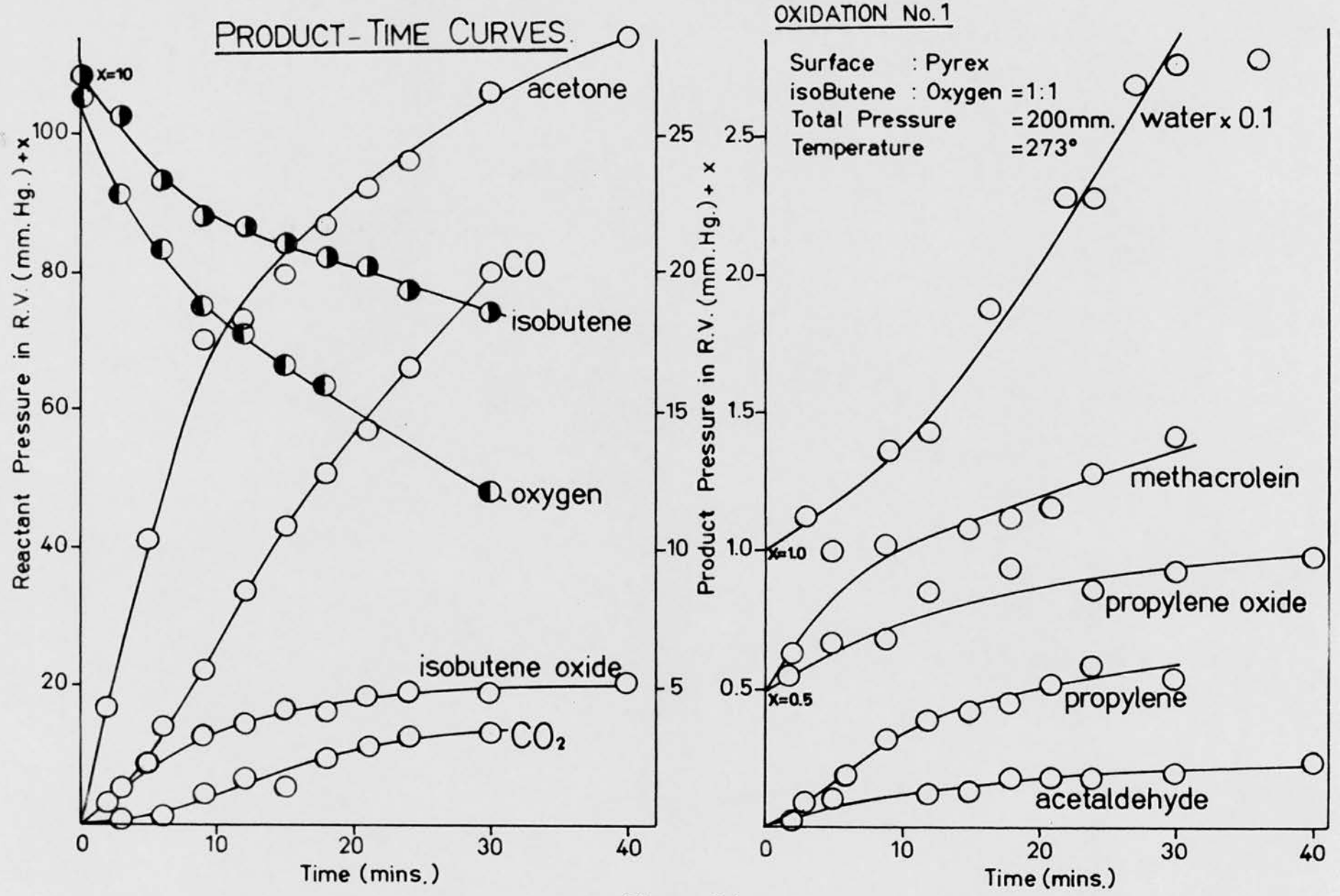

PRODUCT-TIME CURVES.
X=10
acetone
CO
isobutene
oxygen
isobutene oxide
CO_2
Reactant Pressure in R.V. (mm.Hg.) + x
Product Pressure in R.V. (mm.Hg.) + x
Time (mins.)
OXIDATION No. 1
Surface : Pyrex
isoButene : Oxygen = 1:1
Total Pressure = 200mm.
Temperature = 273°
water x 0.1
methacrolein
propylene oxide
propylene
acetaldehyde
X=1.0
X=0.5

Figure C.1.

TABLE No. C.2 (figures C.2., and C.25b.)

OXIDATION No.2

Ratio iC_4H_8: O_2 = 1 : 2 Total Pressure = 318 mm.Hg. Temperature ≠ 273°

Pressure in Reaction Vessel (mm.Hg.)

Time (min.)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6	CH_3CHO	MA
0.0	0.00	216.0	102.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3.0	-0.03	200.0	86.7	3.43	0.38	0.22	-	-	-	-	-	-
6.0	+1.24	177.5	73.3	9.76	1.91	0.31	-	-	-	-	-	-
9.0	3.95	159.3	-	18.6	-	-	-	-	-	-	-	-
12.0	6.32	152.5	53.4	25.7	7.86	0.66	-	-	-	-	-	-
15.0	7.65	147.0	48.1	31.1	-	-	-	-	-	-	-	-
18.0	9.50	138.5	43.9	35.8	10.8	0.79	-	-	-	-	-	-
21.0	11.6	128.9	40.3	41.5	14.4	0.96	-	-	-	-	-	-
24.0	13.5	121.9	37.8	48.4	17.1	-	-	-	-	-	-	-
30.0	17.9	-	31.1	-	21.3	1.29	-	-	-	-	-	-
1.5		-	-	-	-	-	8.90	1.97	-	0.08	tr.	0.12
4.5		-	-	-	-	-	19.0	4.00	-	0.21	0.25	0.51
7.5		-	-	-	-	-	25.1	6.07	-	0.64	0.30	-
12.5		-	-	-	-	-	36.0	5.38	-	-	-	-
16.5		-	-	-	-	-	40.1	6.21	-	0.50	0.35	1.08
19.5		-	-	-	-	-	44.4	6.60	-	0.53	0.43	0.92
22.5		-	-	-	-	-	46.4	5.96	-	0.53	0.47	0.99
28.5		-	-	-	-	-	50.6	6.07	-	0.68	0.52	1.02

Other Products:

Time (min)	HCHO (mm.)
2.1	2.70
4.1	5.21
6.2	8.26
8.2	10.8
12.3	15.4
14.3	17.6
16.4	15.7
20.5	18.0

Time (min)	H_2O (mm)	Time (min)	H_2O (mm)
9.1	11.9	54.6	79.5
21.4	40.4	65.0	87.5
21.8	43.5	65.5	83.0
31.8	57.0	75.0	85.3
32.3	57.1	77.3	93.0
43.2	71.0	87.0	97.1
43.6	70.8	87.4	92.0
54.1	78.0	100.0	102.0

Material Balance:

Time (min)	C	H	O
0	408	816	432
4.5	408	825	426
7.5	409	832	438
12.5	415	789	438
16.5	401	789	444
19.5	408	793	447
22.5	408	793	445
28.5	411	783	450

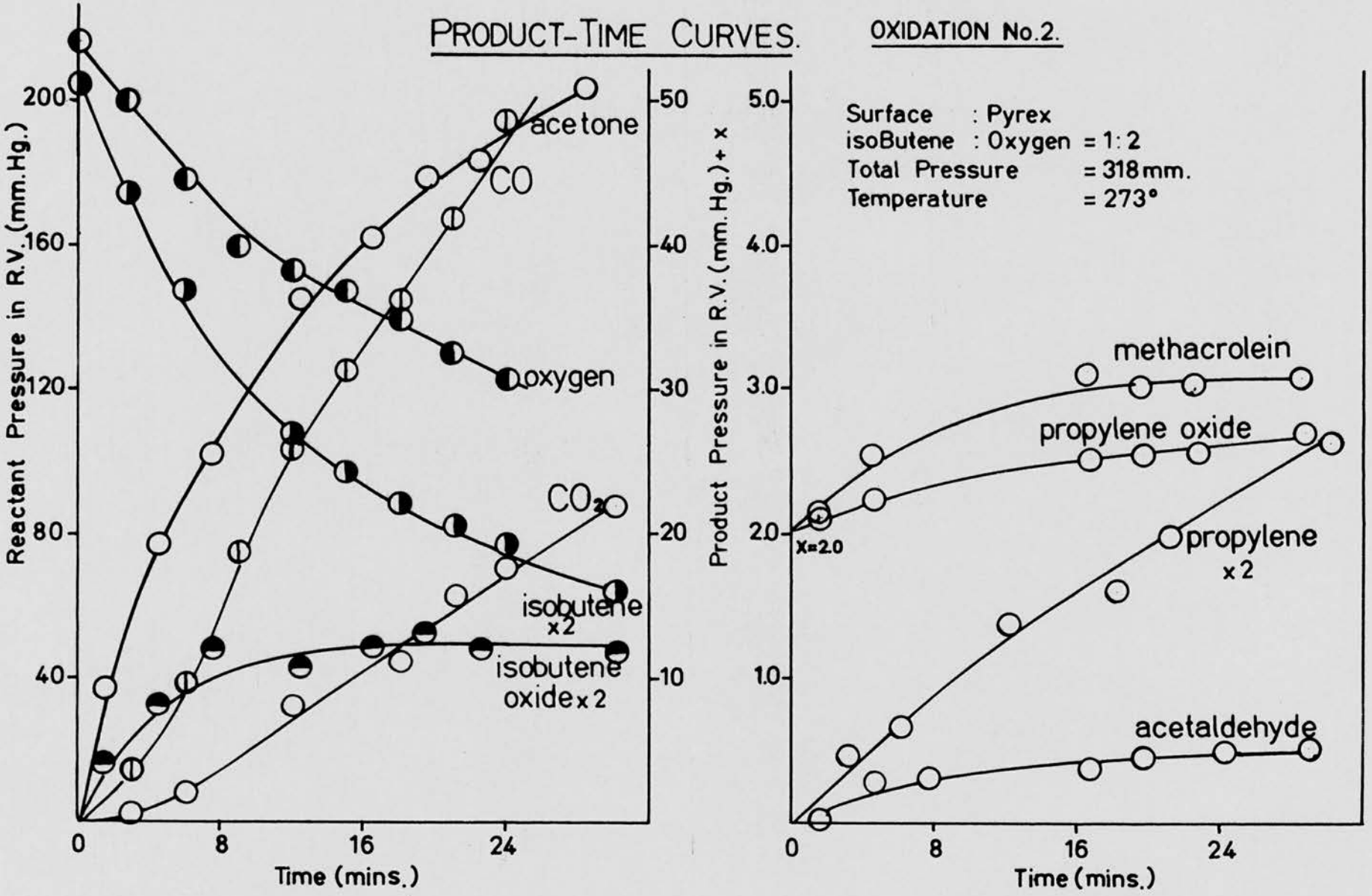

PRODUCT-TIME CURVES.
OXIDATION No.2.
Surface : Pyrex
isoButene : Oxygen = 1:2
Total Pressure = 318 mm.
Temperature = 273°
Reactant Pressure in R.V. (mm.Hg.)
Product Pressure in R.V. (mm.Hg.) + x
Time (mins.)
acetone
CO
oxygen
CO2
isobutene x2
isobutene oxide x 2
methacrolein
propylene oxide
propylene x2
acetaldehyde
X=2.0

Figure C.2.

TABLE No. C.3. (figures C.3. and C.25a.)

OXIDATION No. 3

Ratio iC_4H_8: O_2 = 2 : 1 Total Pressure = 150 mm.Hg. Temperature = 273°

Pressure in Reaction Vessel (mm.Hg.)

Time (min.)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA
0	0.00	51.0	102.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	-0.52	51.0	100.8	0.20	0.02	0.04	1.16	0.28	-	-	-	-
6	-1.48	44.3	99.4	0.66	0.10	0.10	2.75	0.73	-	-	-	-
9	-2.23	42.9	93.6	1.14	0.12	0.17	5.10	1.19	-	-	-	-
12	-2.92	38.1	92.6	2.08	0.42	0.21	6.80	1.53	-	-	-	-
16	-3.61	38.1	86.9	2.64	0.41	0.25	8.59	1.88	-	-	-	-
20	-3.96	32.9	88.6	3.57	0.53	0.35	9.60	2.26	-	-	-	-
25	-3.79	29.4	84.4	4.02	0.94	0.36	11.3	2.43	-	-	-	-
30	-3.20	25.8	80.9	4.32	1.27	0.42	12.7	2.70	-	-	-	-
40	-1.81	23.8	78.8	5.64	1.39	0.51	14.7	2.87	-	-	-	-

Other Products:

Time (min)	HCHO (mm)
2	0.90
4	0.97
5	1.05
8	1.75
10	2.06
12	3.00
15	3.93

Time (min)	H_2O (mm)	Time (min.)	H_2O (mm)
2	0.46	24	11.5
3	0.71	27	13.3
6	1.57	30	13.9
9	4.27	33	14.5
12	4.66	36	16.5
15	8.33	39	17.3
18	8.41	42	18.2
21	8.80	45	18.5

Material Balance:

Time (Min.)	C.	H.	O.
0	410	820	102
3	409	822	106
9	398	799	97
12	404	817	96
16	390	790	103
25	394	801	97
30	387	796	92
40	386	792	98

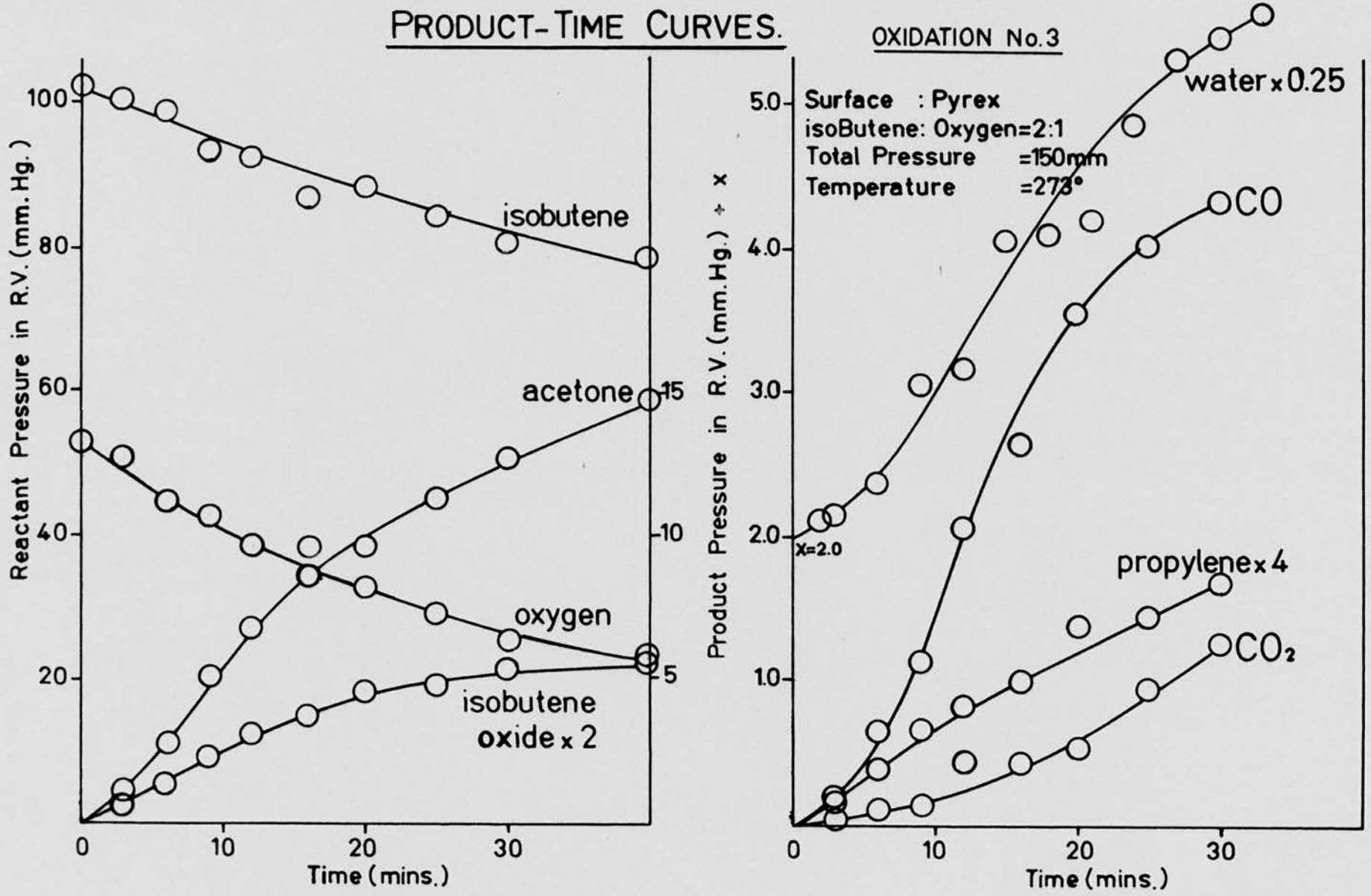

PRODUCT-TIME CURVES.
OXIDATION No.3
Surface : Pyrex
isoButene: Oxygen=2:1
Total Pressure =150mm
Temperature =273°
Reactant Pressure in R.V. (mm. Hg.)
Product Pressure in R.V. (mm.Hg.) ÷ x
Time (mins.)
isobutene
acetone
oxygen
isobutene oxide x 2
water x 0.25
CO
propylene x 4
CO₂
X=2.0

Figure C.3.

TABLE No. C.4. (figures C.4. and C.25d.)

OXIDATION No. 4.

Ratio $iC_4H_8:O_2$ = 1:2 Total Pressure = 150 mm.Hg. Temperature = 273°

Pressure in Reaction Vessel (mm:Hg.)

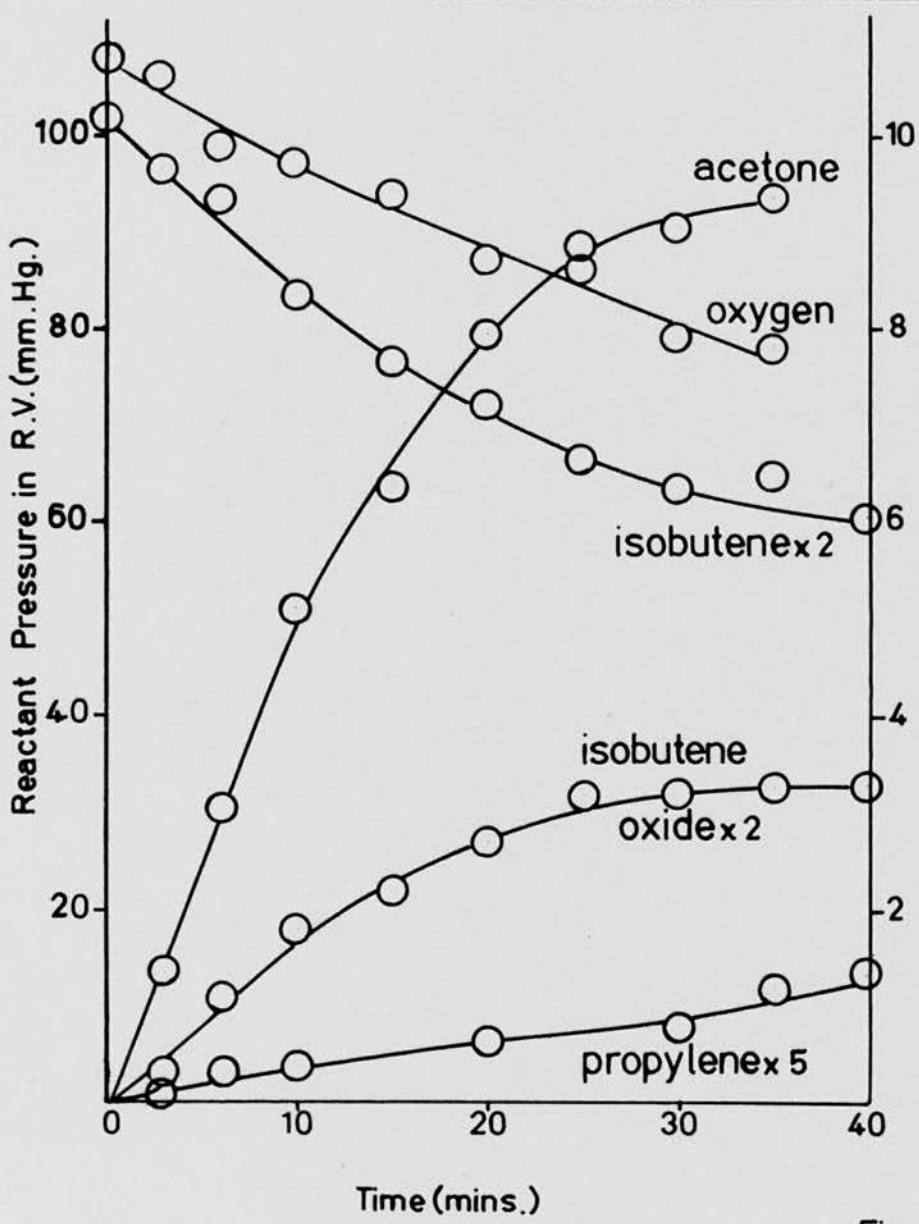
Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA.
0	0.00	108.1	51.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	+0.01	106.5	48.5	0.03	0.02	tr.	1.39	0.18	-	-	-	-
6	0.02	99.0	47.0	0.51	0.10	0.07	3.08	0.54	-	-	-	-
10	0.07	97.8	41.9	1.11	0.47	0.08	5.17	0.90	-	-	-	-
15	0.18	94.1	38.3	2.05	-	-	6.40	1.10	-	-	-	-
20	0.34	87.5	36.2	2.97	0.81	0.13	7.99	1.35	-	-	-	-
25	0.52	87.3	33.4	3.97	-	-	8.89	1.60	-	-	-	-
30	0.63	79.3	32.0	4.60	1.19	0.16	9.06	1.58	-	-	-	-
35	0.82	78.1	32.8	5.17	2.00	0.24	9.40	1.63	-	-	-	-
40	0.99	79.6	30.2	6.09	2.40	0.27	-	1.65	-	-	-	-
50	-	-	-	-	-	-	10.9	1.77	0.43	0.10	0.10	0.32

Other Products :

Time (min)	HCHO (mm)
6	1.66
12	2.88
18	5.24
24	6.18
30	8.32
36	10.0

Time (min)	H_2O (mm)
9	1.39
18	2.41
30	5.19
42	8.55
48	9.69
66	11.0
81	12.3
96	16.9

PRODUCT - TIME CURVES.



OXIDATION No. 4

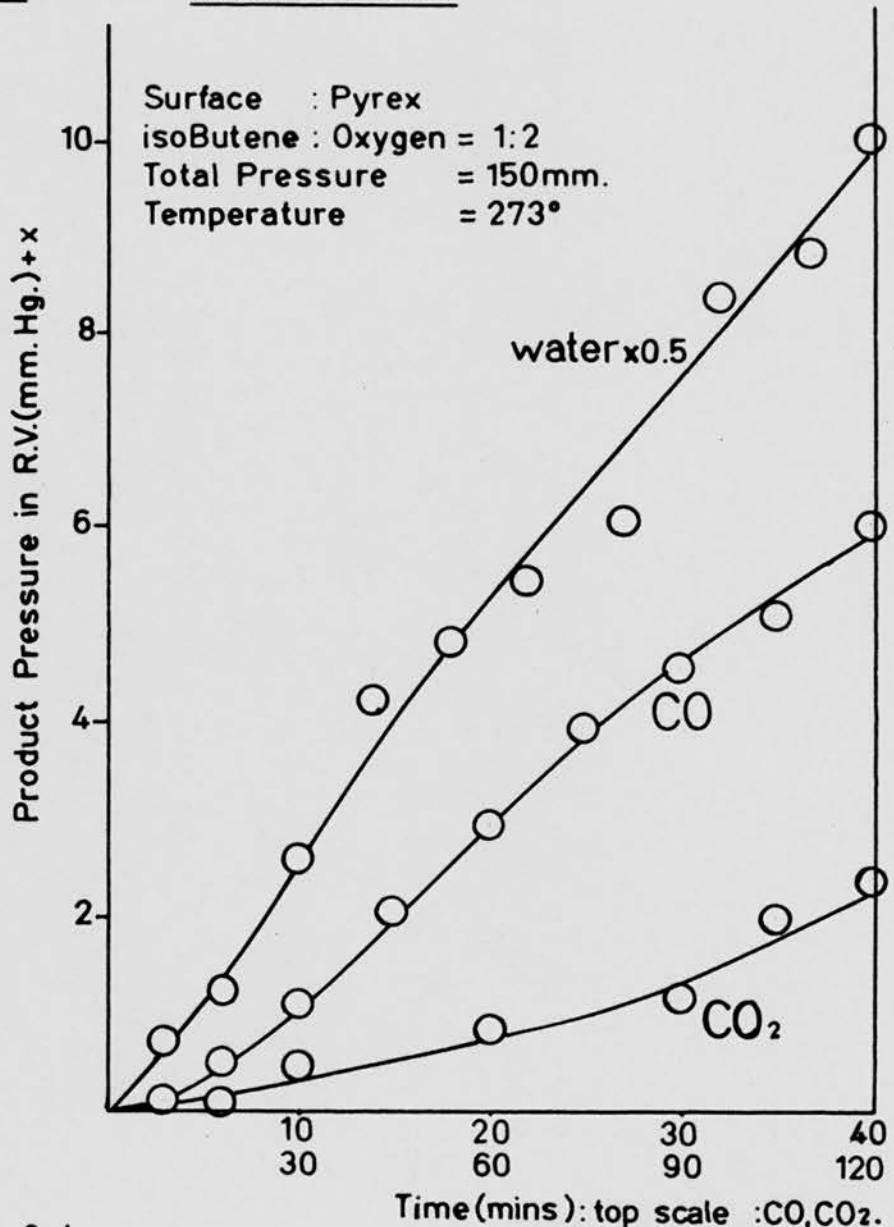


Figure C.4.

TABLE No. C.5. (figures C.5., and C.25c.)

OXIDATION No. 5

Ratio $iC_4H_8:O_2$ = 2 : 1 Total Pressure =300mm.Hg. Temperature = 273°

Pressure in Reaction Vessel (mm.Hg.)

Time (Min.)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA	MeOH	CH_4	HCHO	H_2O
0	0.00	100.8	198.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	-1.07	79.7	179.1	3.61	0.88	0.44	11.8	3.43	0.00	0.26	tr.	-	0.00	0.00	4.28	4.60
6	-1.63	55.3	164.3	9.50	3.18	0.81	25.4	7.00	tr.	0.67	0.14	1.01	tr.	0.00	7.36	8.10
9	-1.28	38.2	151.9	15.0	4.90	1.11	34.6	9.72	0.09	0.92	-	1.49	0.17	0.00	12.2	14.5
12	-0.93	28.8	144.0	19.1	5.67	1.22	38.9	10.4	0.23	0.91	-	1.54	0. 30	0.00	19.2	21.9
15	-0.53	22.6	139.2	22.6	-	1.08	44.3	11.6	0.52	1.04	0.28	1.52	0.63	0.00	21.4	29.2
18	-0.23	16.2	134.8	24.4	4.02	1.21	46.0	12.4	0.36	1.18	0.30	1.82	0.58	0.00	22.6	36.8
21	+0.04	10.6	131.9	26.8	5.91	1.24	50.3	12.5	0.45	1.15	0.44	1.75	0.71	0.00	28.2	40.9
24	0.34	6.6	127.2	27.8	8.14	1.39	52.0	13.1	0.52	1.24	0.34	1.97	0.95	tr.	31.8	45.4
30	0.63	0.9	122.8	30.7	8.85	1.47	55.0	13.4	0.64	1.35	0.59	1.82	-	0.16	-	45.5
10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	19.1
27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	31.1	45.4

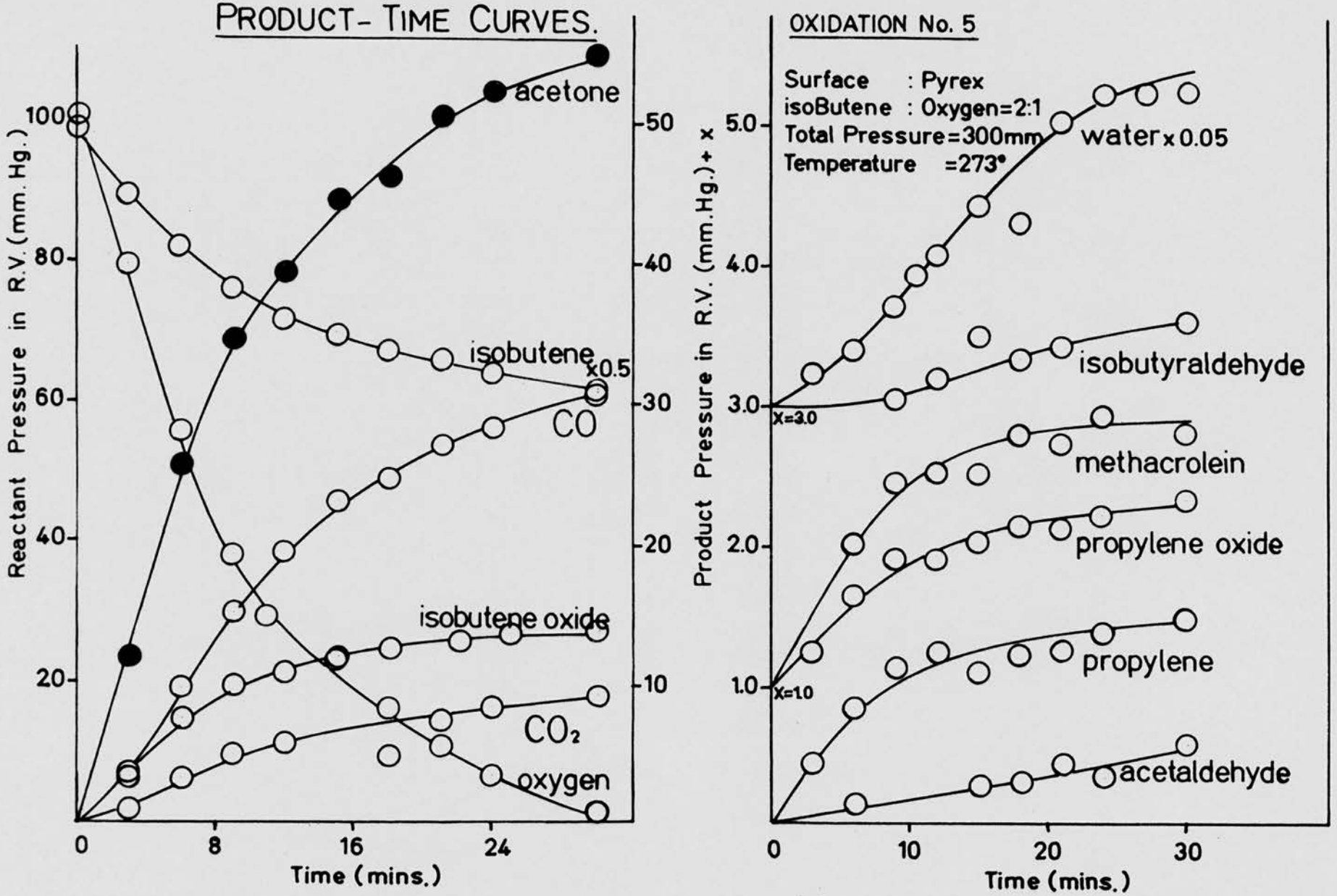

PRODUCT- TIME CURVES.
Reactant Pressure in R.V. (mm. Hg.)
Time (mins.)
acetone
isobutene
x0.5
CO
isobutene oxide
CO_2
oxygen
OXIDATION No. 5
Surface : Pyrex
isoButene : Oxygen=2:1
Total Pressure=300mm
Temperature =273°
Product Pressure in R.V. (mm.Hg.)+ x
water x 0.05
isobutyraldehyde
X=3.0
methacrolein
propylene oxide
propylene
X=1.0
acetaldehyde
Time (mins.)

Figure C.5.

TABLE No. C. 6. (fig. C. 6.)

OXIDATION No. 6

Ratio $iC_4H_8:O_2$ = 1:1 Total Pressure = 200 mm. Hg. Temperature = 273°

Pressure in Reaction Vessel (mm. Hg.)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA	MeOH	CH_4
20	+2.00	-	72.1	13.3	4.37	0.67	22.5	5.01	tr.	0.34	-	0.79	tr.	tr.
30	3.26	52.4	67.1	18.3	6.55	0.77	28.0	5.66	-	0.42	-	0.86	0.50	tr.
40	4.60	41.9	64.0	22.9	8.65	0.94	31.8	6.45	-	0.41	-	-	-	tr.
50	5.89	36.0	60.3	28.6	10.9	1.15	36.1	6.69	0.20	0.64	-	0.97	-	tr.
60	7.29	26.7	57.4	34.0	12.9	1.28	39.8	7.44	-	0.72	-	1.12	0.82	0.10
70	8.85	17.1	54.3	37.7	-	1.48	-	-	-	-	-	-	-	0.24
80	10.3	10.0	51.8	45.1	16.5	1.72	45.8	6.82	0.27	0.77	-	1.11	1.53	0.20
100	12.2	5.24	48.2	51.1	17.0	2.03	51.0	6.32	1.02	0.79	-	1.34	1.77	0.45
120	12.2	5.09	48.5	52.9	17.3	1.87	51.4	6.12	1.01	0.88	-	1.31	1.84	-
150	12.0	3.97	47.9	51.2	16.8	1.95	51.2	5.41	1.10	0.90	-	1.12	1.90	0.48

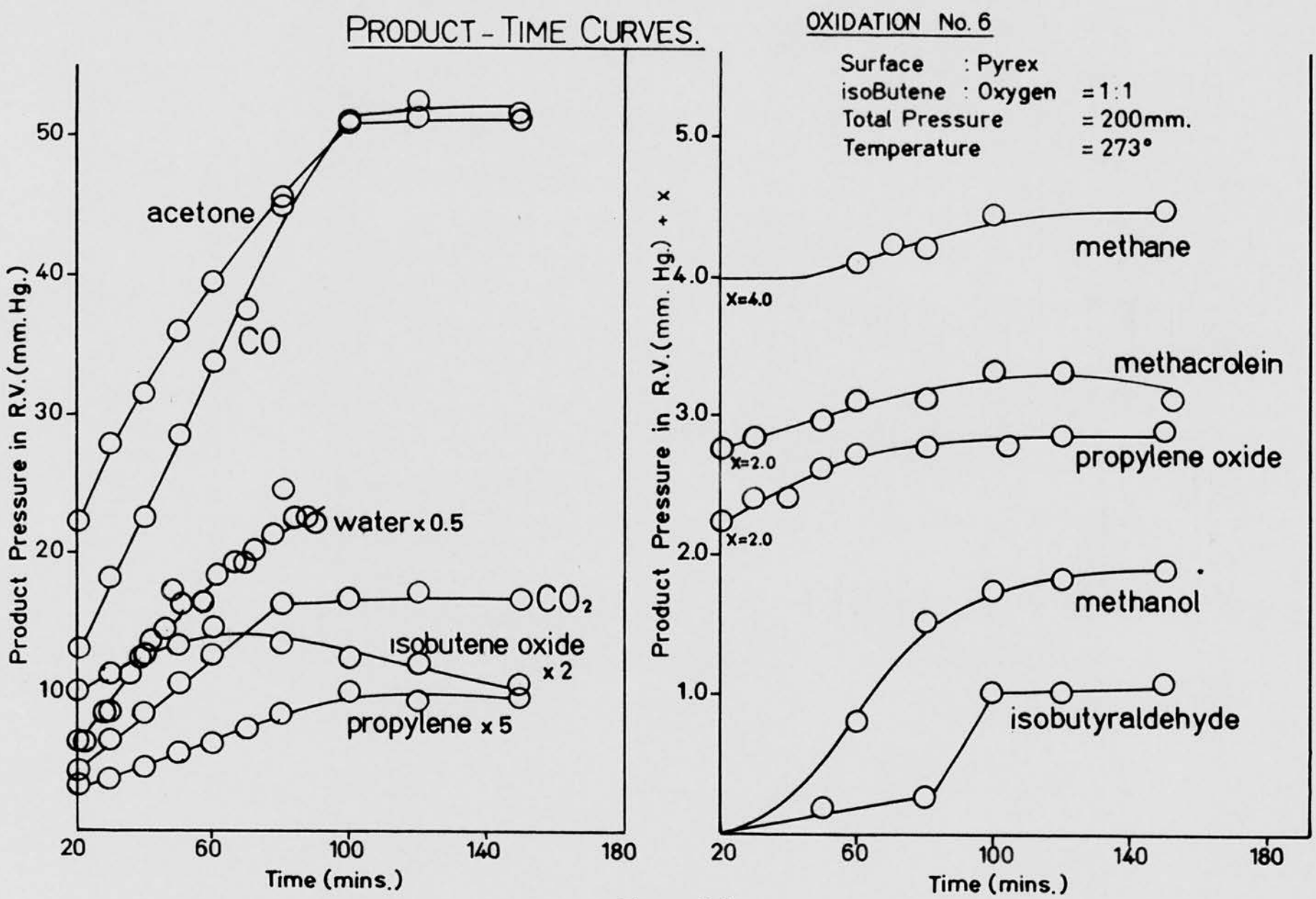

PRODUCT - TIME CURVES.
OXIDATION No. 6
Surface : Pyrex
isoButene : Oxygen = 1:1
Total Pressure = 200mm.
Temperature = 273°
Product Pressure in R.V.(mm.Hg.)
Time (mins.)
acetone
CO
water x 0.5
CO_2
isobutene oxide x 2
propylene x 5
Product Pressure in R.V.(mm. Hg.) + x
methane
X=4.0
methacrolein
X=2.0
propylene oxide
X=2.0
methanol
isobutyraldehyde

Figure C.6.

2.2 The effect of temperature

The effect on the product distribution of varying the temperature of 1:1 mixtures of isobutene: oxygen was studied in Oxidation No. 1 and Nos. 7 - 13, covering a temperature range of 246° - 352°.

As the reaction was not conveniently measurable over the whole range at a constant initial pressure, the pressure was adjusted to suit the conditions, and varied from 300 mm. Hg. at 246° to 120 mm. Hg. at 352°. The table of results and product/time plot for Oxidation No. 1 has been given in section 2.1. This section includes the rest of the series.

TABLE No. C.7. (fig. C.7)

OXIDATION No. 7

Ratio $iC_4H_8 : O_2$ = 1:1 Total Pressure = 210 mm.Hg. Temperature = 283°

Pressure in Reaction Vessel (mm.Hg.)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA	MeOH
0	0.00	108.0	102.9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	-0.16	94.1	88.6	2.54	0.85	0.25	11.2	2.41	0.00	0.16	0.00	-	0.00
6	+0.56	83.4	80.0	5.55	1.71	0.36	17.7	3.74	0.00	0.38	0.00	0.26	0.00
9	0.95	72.4	74.9	7.96	2.58	0.44	21.2	4.31	tr.	0.40	0.00	0.69	0.00
12	1.36	67.5	73.0	10.2	3.31	0.60	23.2	4.85	tr.	0.48	0.00	0.87	tr.
15	1.83	63.0	68.5	13.1	4.16	0.76	23.8	5.25	-	0.45	0.00	0.85	tr.
18	2.31	58.4	70.1	15.6	5.20	0.83	-	-	-	-	-	-	-
21	2.79	51.4	64.8	16.9	6.02	0.86	29.5	5.80	0.29	0.60	tr.	0.86	tr.
24	3.33	49.0	63.0	19.7	6.80	0.98	30.4	6.17	0.35	0.62	tr.	1.00	0.91
30	4.62	38.5	60.5	25.5	9.06	1.16	34.4	6.35	-	0.66	0.10	1.00	-
40	7.32	-	-	-	-	-	41.0	6.92	0.37	0.93	0.45	1.15	1.22

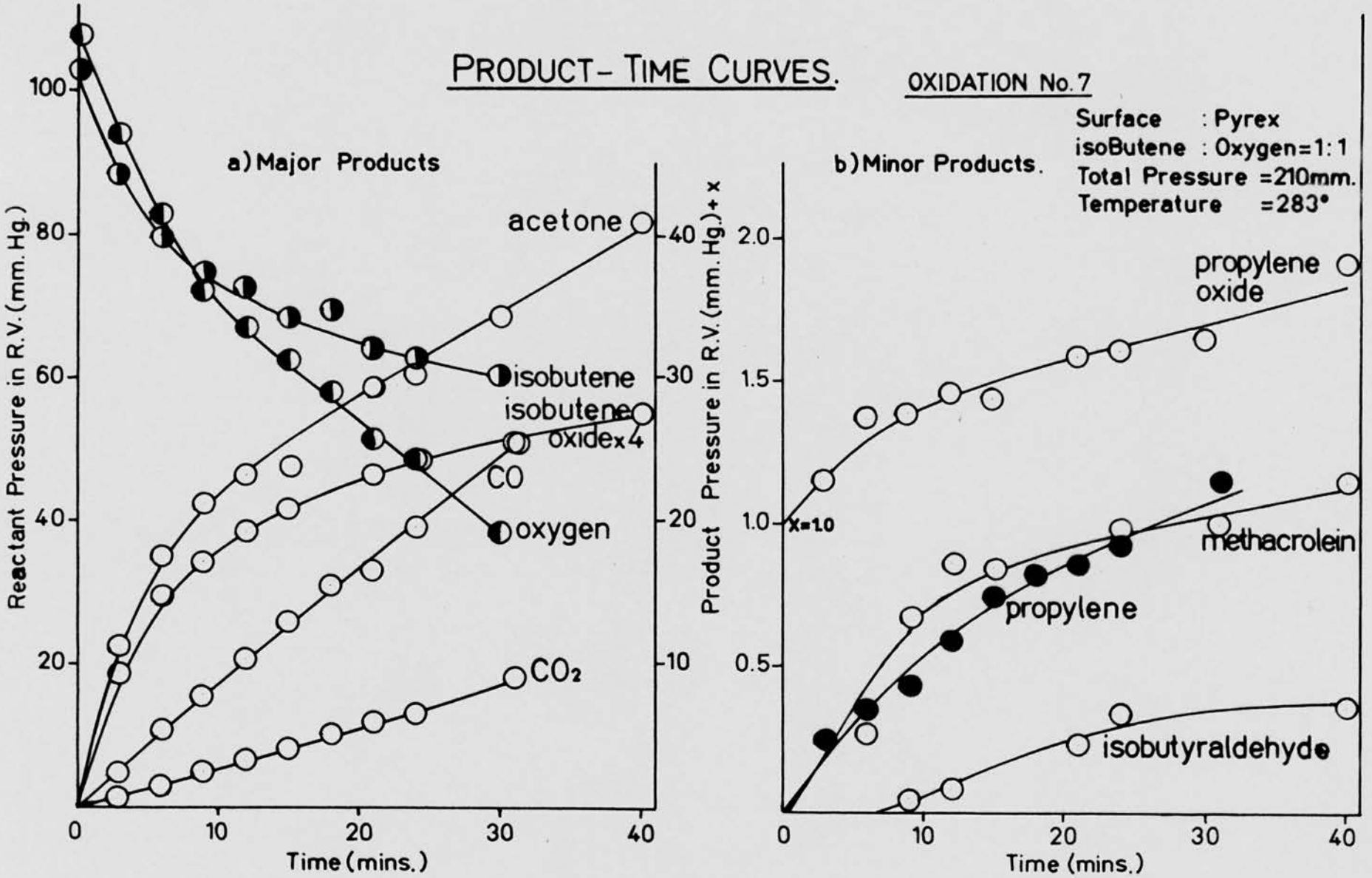

PRODUCT- TIME CURVES.
OXIDATION No.7
Surface : Pyrex
isoButene : Oxygen=1:1
Total Pressure =210mm.
Temperature =283°
a) Major Products
b) Minor Products.
Reactant Pressure in R.V.(mm.Hg.)
Product Pressure in R.V.(mm.Hg.)+x
Time (mins.)
acetone
isobutene
isobutene oxide x4
CO
oxygen
CO2
propylene oxide
methacrolein
propylene
isobutyraldehyde
X=1.0

Figure C.7.

TABLE No. C. 8 (fig. C8a, b.)

OXIDATION No.8

Ratio $iC_4H_8 : O_2$ = 1 : 1 Total Pressure = 206 mm.Hg. Temperature = 293°

Pressure in Reaction Vessel (mm.Hg.)

Time (min)	ΔP mm. Hg	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA
0.0	0.0	103.0	103.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.4	-0.27	88.2	86.4	3.97	1.16	0.37	-	-	-	-	-	-
4.5		83.6	81.7	5.71	1.45	0.53	-	-	-	-	-	-
4.8	-0.10	80.3	76.5	7.00	1.91	0.53	-	-	-	-	-	-
6.7	+0.31	72.4	-	8.59	2.89	0.58	-	-	-	-	-	-
8.9	0.72	67.1	70.4	11.6	3.46	0.78	-	-	-	-	-	-
9.0		65.4	72.5	11.4	3.38	0.85	-	-	-	-	-	-
11.1		62.0	67.4	14.0	4.45	0.93	-	-	-	-	-	-
12.9		55.0	68.8	16.4	5.78	1.10	-	-	-	-	-	-
13.3	2.04	51.1	67.6	17.6	5.48	1.25	-	-	-	-	-	-
15.0		49.8	63.9	19.6	6.43	1.22	-	-	-	-	-	-
15.6	2.51	44.5	65.5	22.6	6.96	1.23	-	-	-	-	-	-
17.5		41.8	58.0	24.1	8.58	1.42	-	-	-	-	-	-
17.8		39.1	60.1	26.7	8.64	1.60	-	-	-	-	-	-
19.6	5.40	33.8	56.5	30.4	10.3	1.71	-	-	-	-	-	-
22.2		21.7	-	36.0	12.1	1.94	-	-	-	-	-	-
22.5		21.9	52.7	37.2	13.3	1.99	-	-	-	-	-	-
26.0	9.70	8.60	48.0	50.5	15.8	2.27	-	-	-	-	-	-
27.7		4.23	-	52.2	14.7	2.44	-	-	-	-	-	-
2.0	-0.27	-	-	-	-	-	9.37	2.08	tr.	0.22	0.04	0.30
2.8		-	-	-	-	-	11.2	2.38	-	0.20	-	0.32
4.0	-0.10	-	-	-	-	-	13.4	2.80	0.26	0.24	0.07	0.42
4.8		-	-	-	-	-	14.6	3.14	-	0.26	-	0.65
6.0	+0.31	-	-	-	-	-	16.1	3.52	0.41	0.27	0.11	0.77
7.3		-	-	-	-	-	20.4	-	-	0.32	-	-
8.0	0.72	-	-	-	-	-	19.1	3.98	0.65	0.41	0.28	0.99
9.6		-	-	-	-	-	21.4	4.80	-	0.48	-	0.88
10.0	1.37	-	-	-	-	-	21.6	4.27	0.68	0.36	0.26	0.79
11.9		-	-	-	-	-	24.8	5.22	-	0.67	-	0.81
12.0	2.04	-	-	-	-	-	25.7	5.10	0.84	0.44	0.30	0.92
14.0	2.51	-	-	-	-	-	28.3	5.62	0.87	0.54	0.44	1.12

OXIDATION No.8 (Cont.)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA
14.2		-	-	-	-	-	28.2	5.50	-	0.71	-	1.06
16.2		-	-	-	-	-	32.8	6.45	-	0.68	-	1.18
17.0	3.88	-	-	-	-	-	32.5	6.14	1.16	0.66	0.54	1.29
19.3		-	-	-	-	-	37.2	7.56	-	0.89	-	1.30
20.0	5.59	-	-	-	-	-	37.5	6.86	1.16	0.74	0.75	1.25
22.0		-	-	-	-	-	42.1	7.90	-	1.11	-	1.50
25.0	9.00	-	-	-	-	-	46.6	6.88	1.48	1.05	1.12	1.85
26.4		-	-	-	-	-	49.6	8.20	-	1.30	-	-

TABLE NO. C.8.a. (figs. C.8., C.26.)

OXIDATION NO. 8 Other Products:-

Total Pressure (mm. Hg.)	Time (min.)	HCHO (mm.)	CO (mm.)	Me_2CO (mm.)
206	0.6	3.06		
	0.6	3.10		
	0.6	2.94		
	1.2	4.80	1.91	
	1.2	4.42		
	2.4	6.90	3.17	
	2.4	6.21		
	2.4	6.50		
	2.4	6.33		
	3.7	8.15	5.46	
	3.7	9.24		
	5.0	9.80	7.04	
	5.0	10.0		
	5.0	9.87		
	5.0	8.90		
	5.6	10.5		
	7.8	13.7		
	7.8	13.5		
	7.8	13.2		
180	2.0	4.27		6.97
	4.0	5.95		11.8
	6.0	8.42		17.0
150	3.0	4.30		6.44
	3.0	3.98		
122	5.0	2.36		2.88

Time (min.)	H_2O (mm.)	Time (min.)	H_2O (mm.)
1.5	3.97	18.0	25.9
3.0	5.66	21.0	28.7
3.75	5.47	22.5	29.9
4.5	5.50	24.0	31.6
6.0	9.70	25.5	36.6
7.5	9.97	27.0	34.7
9.0	12.4	28.5	38.4
10.5	15.4	30.0	38.2
12.0	17.2	31.5	42.1
14.5	19.3	33.0	43.0
15.0	22.2	38.25	44.6

Material Balance:

Time	C	H	O
0	412	824	206
2	395	791	205
4	398	795	204
6	396	799	204
8	393	790	206
10	404	816	213
12,	416	840	202

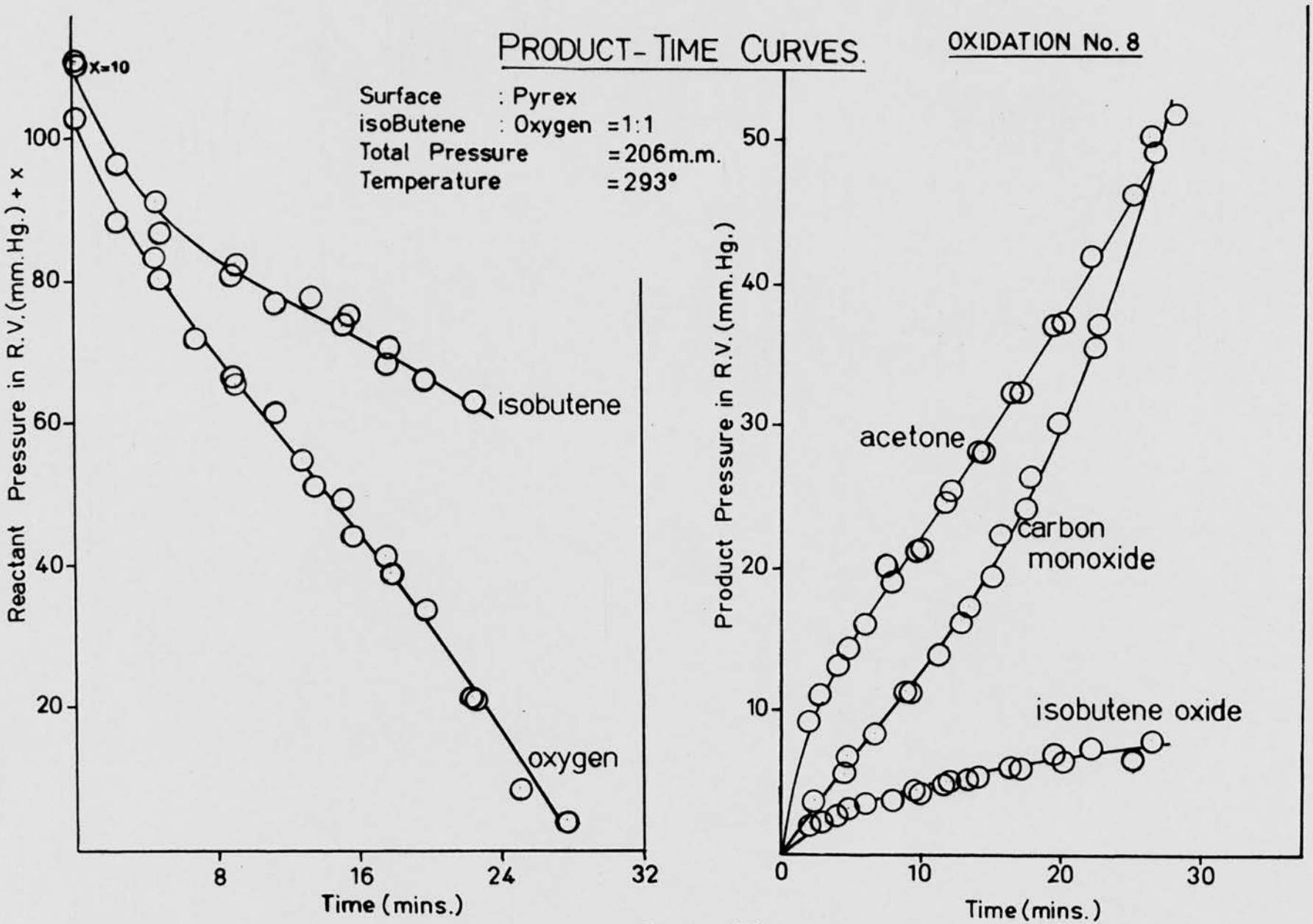

PRODUCT-TIME CURVES.
OXIDATION No. 8
Surface : Pyrex
isoButene : Oxygen =1:1
Total Pressure =206m.m.
Temperature =293°
X=10
Reactant Pressure in R.V.(mm.Hg.) + x
100
80
60
40
20
isobutene
oxygen
8
16
24
32
Time (mins.)
Product Pressure in R.V.(mm.Hg.)
50
40
30
20
10
acetone
carbon monoxide
isobutene oxide
0
10
20
30
Time (mins.)

Figure C.8.a.

PRODUCT-TIME CURVES.

OXIDATION No. 8

Surface : Pyrex
isoButene : Oxygen = 1:1
Total Pressure = 206mm.
Temperature = 293°

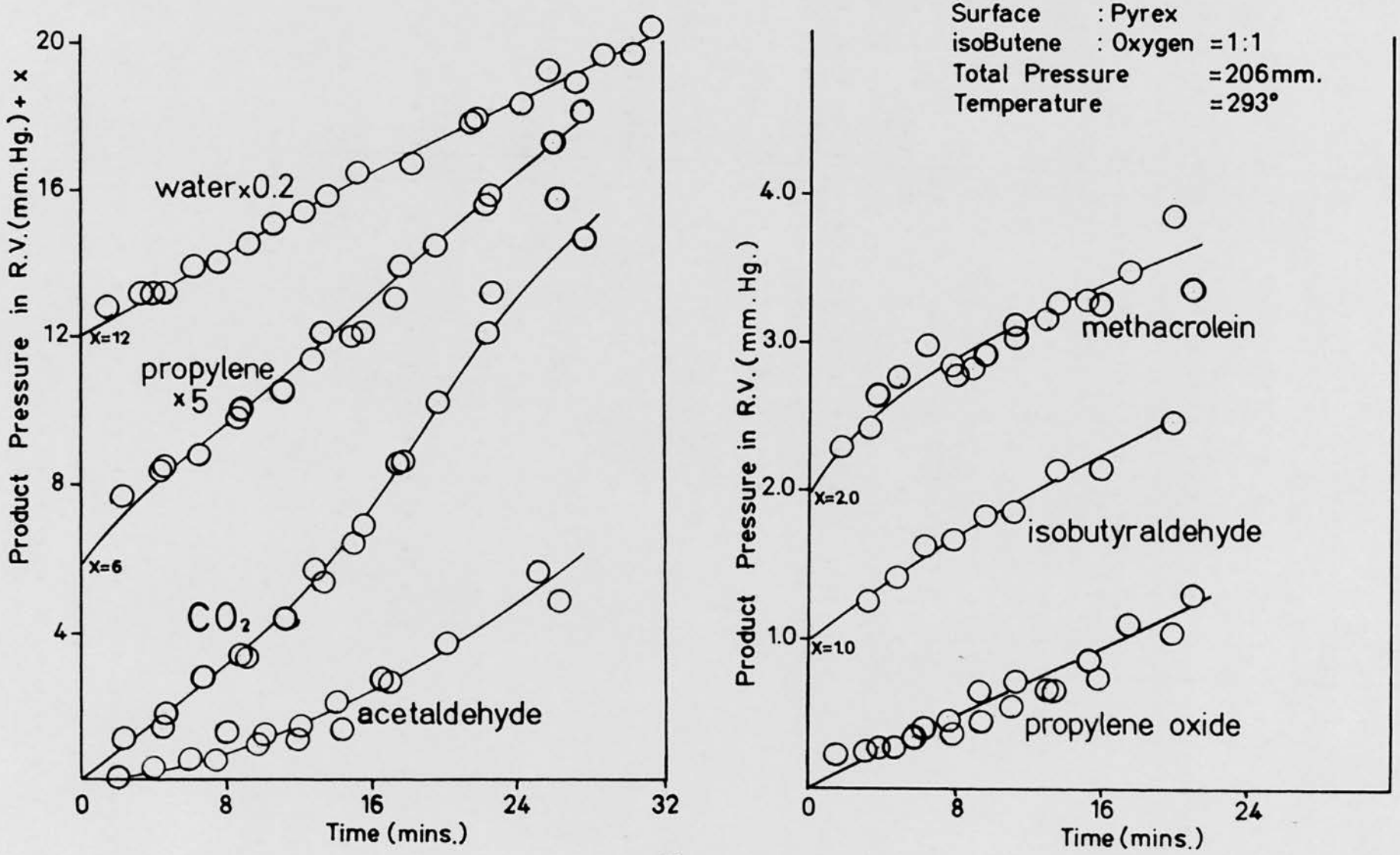


Figure C.8.b.

TABLE No. C. 9. (Fig. C. 9.)

OXIDATION No. 9.

Ratio $iC_4H_8:O_2$ = 1:1 Total Pressure = 220 mm. Hg. Temperature = 303°

Pressure in Reaction Vessel (mm. Hg.)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	C_2H_5CHO	MA	CH_4	CH_3OH
0	0.00	110.0	106.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	-0.14	86.8	90.0	4.53	1.20	0.42	12.3	2.58	0.26	0.20	0.05	0.00	0.55	0.00	0.00
4	+0.35	74.5	77.6	7.33	2.20	0.70	17.6	3.47	0.43	0.41	-	0.00	0.73	0.00	0.00
6	1.14	63.9	72.3	11.6	3.56	0.77	22.7	4.94	0.53	0.39	0.21	0.00	0.82	0.00	0.00
8	2.05	55.0	64.1	17.6	5.03	1.12	28.1	5.68	0.69	0.60	0.41	0.00	1.02	0.00	0.00
10	3.83	41.2	58.6	23.2	7.17	1.36	33.3	6.98	0.74	0.75	0.59	0.00	1.26	0.00	0.00
12	6.20	17.5	57.4	-	9.72	1.81	38.5	7.45	1.01	1.04	0.69	0.00	1.65	tr.	tr.
14	8.62	17.0	49.9	42.7	12.4	2.18	46.5	8.76	1.10	1.16	0.91	tr.	1.51	0.15	0.17
16	-	-	-	-	-	-	47.2	8.87	1.24	1.30	1.08	-	1.78	-	-
17	11.7	2.0	48.9	55.1	15.4	2.76	-	-	-	-	-	-	-	0.06	-
18	-	-	-	-	-	-	49.1	8.67	1.50	1.35	1.14	0.08	-	-	2.10
20	11.9	0.4	45.9	56.2	15.0	2.75	51.1	7.50	1.96	1.38	0.98	-	1.61	0.77	2.20

TABLE NO. C. 9a (figs. C. 9., C. 27a, b.)

OXIDATION NO. 9 Other Products.

Total Press (mm.)	Time (min.)	HCHO (mm.)	Me_2CO (mm.)	Time (min.)	H_2O (mm.)
150	1.0	1.19	1.22	1.5	3.72
	3.0	2.14	2.83		
	5.0	3.36	4.34	2.3	5.60
220	0.5	2.66			
	1.0	4.08	7.24	3.1	7.40
	1.0	3.12			
	1.0	4.10		4.6	10.7
	1.0	3.70			
	2.0	6.01		7.7	17.1
	2.5	5.89			
	3.0	6.65	15.1	10.0	31.0
	3.0	7.01			
	4.0	8.47		11.0	34.0
	4.0	8.33			
	4.5	8.90		15.0	48.0
	5.0	9.01	22.9		
	5.0	9.08		15.0	50.9
	5.0	9.56			
	8.5	12.9		20.0	46.3

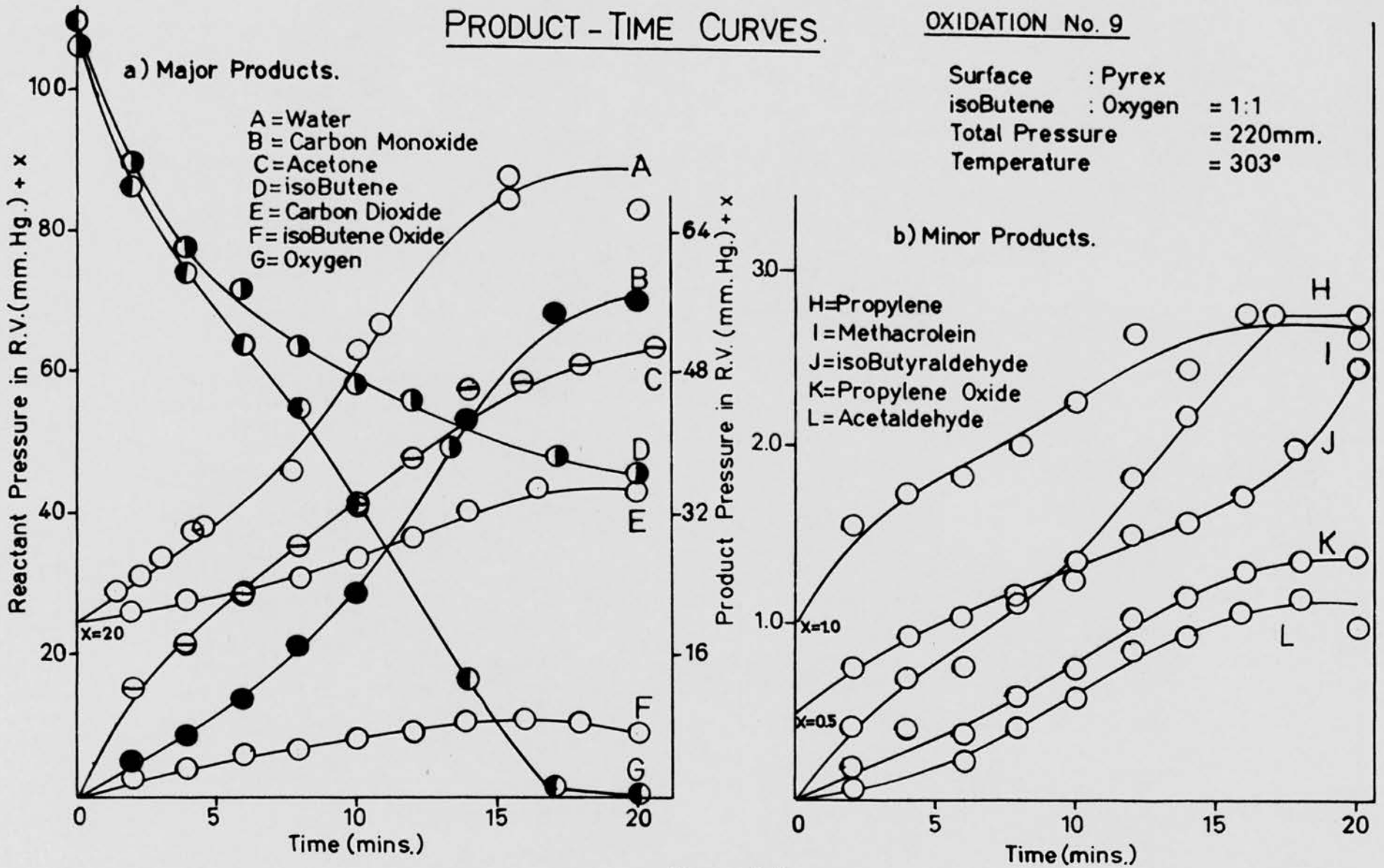

PRODUCT - TIME CURVES.
OXIDATION No. 9
Surface : Pyrex
isoButene : Oxygen = 1:1
Total Pressure = 220mm.
Temperature = 303°
a) Major Products.
A = Water
B = Carbon Monoxide
C = Acetone
D = isoButene
E = Carbon Dioxide
F = isoButene Oxide
G = Oxygen
Reactant Pressure in R.V.(mm.Hg.) + x
Product Pressure in R.V. (mm.Hg.) + x
X=20
Time (mins.)
b) Minor Products.
H = Propylene
I = Methacrolein
J = isoButyraldehyde
K = Propylene Oxide
L = Acetaldehyde
X=1.0
X=0.5
Time (mins.)

Figure C.9.

TABLE No.C.10 (fig. C.10)

OXIDATION No.10

Ratio iC_4H_8: O_2 = 1:1 Total Pressure = 150 mm.Hg. Temperature = 322°

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA
0.0	0.00	77.9	75.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0	-0.13	-	-	-	-	-	2. 02	0.52	0.05	0.04	tr.	tr.
3.0	-0.13	-	-	-	-	-	4.63	0.95	0.15	0.08	0.04	0.11
5.0	0.00	-	-	-	-	-	6.89	1.50	0.37	0.12	0.08	0.25
7.0	+0.60	-	-	-	-	-	9.44	1.94	0.58	0.17	0.16	0.30
9.0	1.48	50.3	-	7.12	-	-	13.3	2.85	0.64	0.29	0.21	0.50
11.0	3.17	-	-	-	-	-	18.5	3.67	0.77	0.42	0.42	0.71
13.0	5.77	-	-	-	-	-	23.1	4.86	0.96	0.58	0.58	0.99
15.0	8.67	-	-	-	-	-	29.2	5.12	0.99	0.80	0.81	1.10
17.0	10.2	-	37.3	-	10.4	3.08	31.0	4.76	1.39	-	-	1.12
19.0	10.2	-	36.4	-	11.5	3.34	31.7	4.18	1.69	0.93	0.89	1.22
2.7		68.2	69.3	1.67	0.63	0.32	-	-	-	-	-	-
5.3		61.5	64.2	2.90	1.27	0.56	-	-	-	-	-	-
7.1		52.9	-	4.49	-	-	-	-	-	-	-	-
10.5		41.6	-	11.0	-	-	-	-	-	-	-	-
12.0		33.2	-	16.2	-	-	-	-	-	-	-	-
13.6		20.4	-	24.7	-	-	-	-	-	-	-	-
15.8		4.38	-	35.2	-	-	-	-	-	-	-	-
7.8		-	57.4	-	2.06	0.89	-	-	-	-	-	-
10.0		-	53.9	-	3.41	1.24	-	-	-	-	-	-
12.2		-	43.8	-	5.42	1.78	-	-	-	-	-	-
14.4		-	42.5	-	8.05	2.52	-	-	-	-	-	-

TABLE NO. C. 10a (figs. C. 10., C. 28b.)

OXIDATION NO. 10 Other Products

Time (min.)	HCHO (mm.)
0.6	1.18
0.6	1.58
1.2	2.40
2.4	3.84
2.4	3.12
3.1	3.60
3.6	4.75
4.8	5.12
4.8	5.06
6.0	5.12
6.0	5.70
6.0	5.09
7.2	5.95

Time (min.)	C_2H_5CHO	CH_4
7.0	0.00	-
9.0	tr.	-
11.0	tr.	-
13.0	tr.	-
15.0	0.05	-
17.0	0.07	-
19.0	0.09	-
10.5	-	0.00
12.0	-	0.06
13.6	-	0.24
15.8	-	0.59

Time (min.)	H_2O (mm.)
1.6	1.76
1.6	2.09
2.5	2.98
3.3	3.16
3.3	4.20
3.3	4.47
4.1	4.12
4.9	4.96
4.9	5.26
6.5	8.00
8.2	11.4
8.2	14.7
9.0	16.0
10.6	23.4
11.5	30.0
12.3	23.9
14.7	36.7
15.5	41.2
17.2	43.7

Material Balance:

Time	C	H	O
0	302	604	156
2	303	611	164
4	299	601	150
6	296	594	150
8	291	590	150
10	296	604	148

PRODUCT - TIME CURVES.

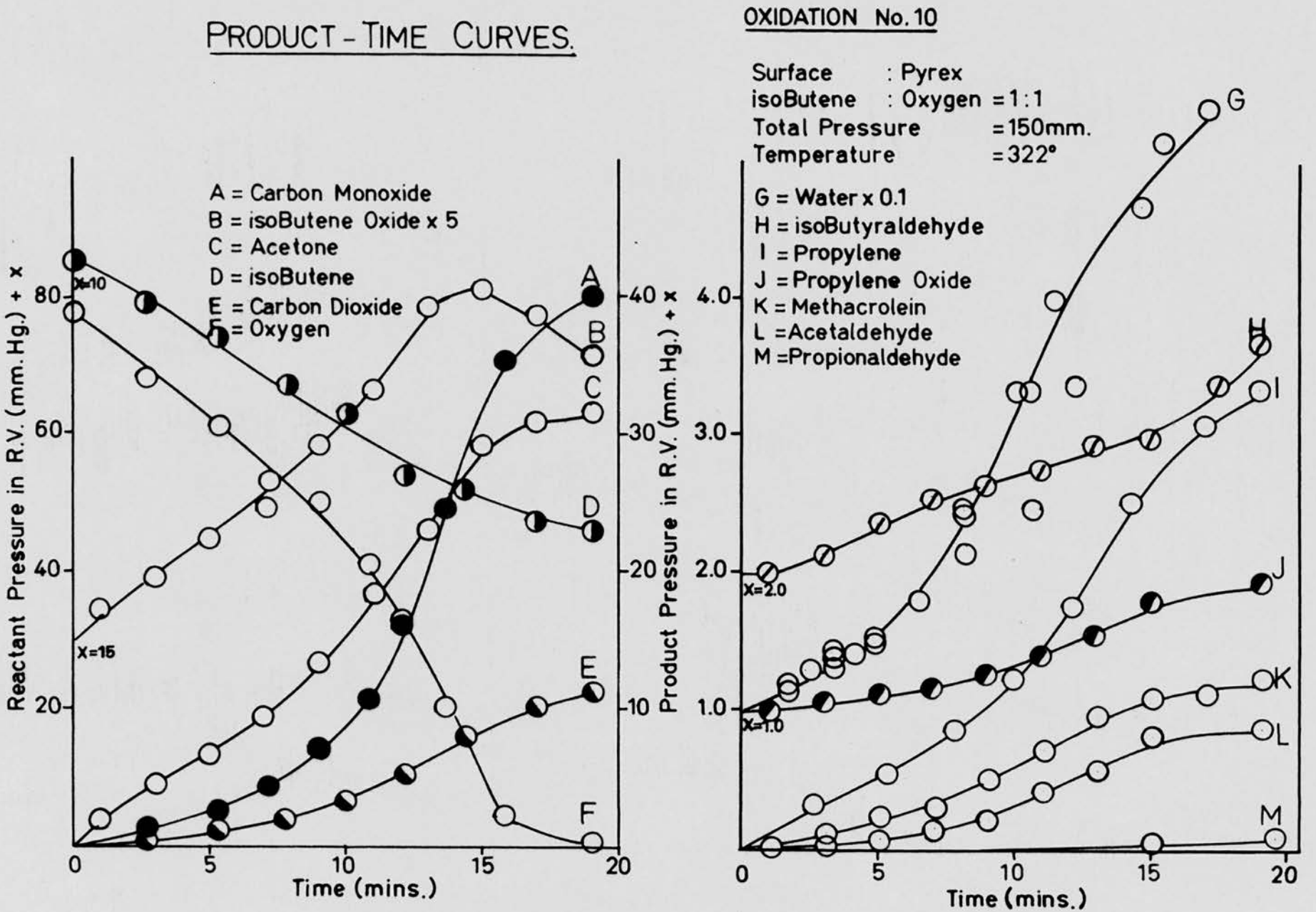


Figure C. 10.

TABLE No. C. 11 (fig. C. 11.)

OXIDATION No. 11

Ratio $iC_4H_8:O_2$ = 1:1 Total Pressure = 150 mm. Hg. Temperature = 337°

Pressure in Reaction Vessel (mm. Hg.)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	C_2H_5CHO	MA	CH_4
0.0	-0.00	75.1	75.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0	-0.05	69.5	70.2	1.32	0.37	0.19	2.96	0.66	0.28	0.08	0.04	0.00	0.09	0.00
1.5	+0.11	65.5	67.0	1.23	0.49	0.21	3.51	0.77	0.25	0.06	-	tr	0.14	0.00
3.0	+0.16	61.0	62.2	2.95	0.87	0.46	6.15	1.20	0.43	0.13	0.14	0.04	0.41	-
3.0	+0.19	55.6	62.0	3.24	1.12	0.47	6.38	1.41	0.53	0.12	0.19	0.04	0.48	tr.
5.0	1.08	52.1	56.0	6.24	1.75	0.84	10.1	1.95	0.75	0.18	0.22	-	0.67	-
5.0	1.10	49.1	55.1	6.67	2.00	0.92	11.0	2.35	0.88	0.28	0.25	-	0.66	tr.
7.0	-	37.1	48.0	13.4	3.67	1.56	15.5	3.13	0.93	0.41	0.38	0.04	0.91	-
7.2	3.79	31.4	45.9	14.2	4.38	1.74	17.4	3.78	0.88	0.45	0.37	0.06	0.92	0.29
9.0	-	17.6	39.1	27.1	7.08	2.56	23.3	4.63	1.03	0.63	0.63	0.11	1.10	0.42
9.4	8.93	10.6	36.5	27.2	7.99	2.74	25.9	5.73	1.00	0.88	0.81	0.10	1.39	0.61

PRODUCT-TIME CURVES.

OXIDATION No.11

Surface : Pyrex
isoButene : Oxygen = 1:1
Total Pressure = 150mm.
Temperature = 337°

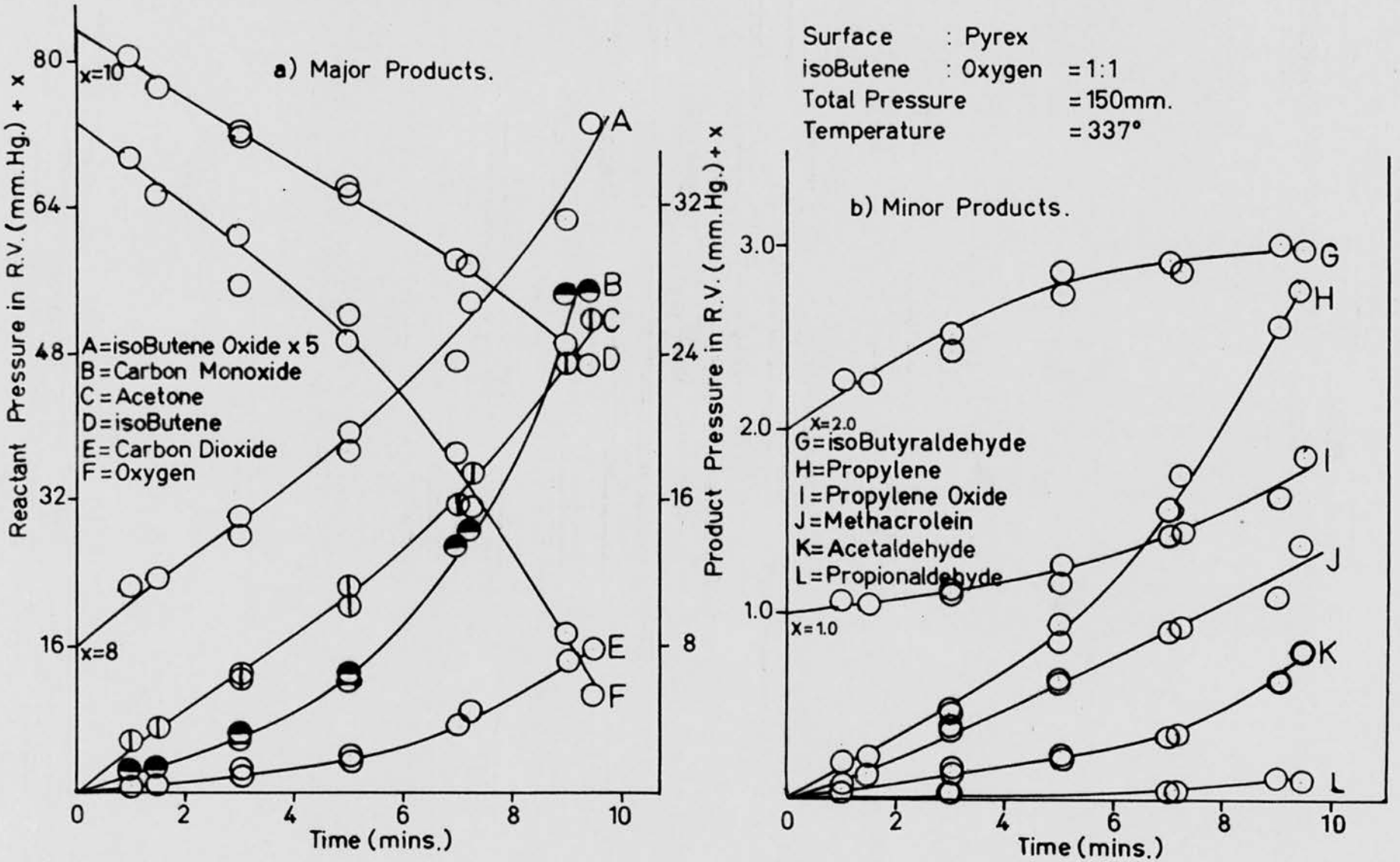


Figure C. 11.

TABLE No. C. 12 (fig. C. 12.)

OXIDATION No. 12

Ratio $iC_4H_8:O_2$ = 1:1 Total Pressure = 120 mm. Hg. Temperature = 352°

Pressure in Reaction Vessel (mm. Hg.)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	C_2H_5CHO	MA	CH_4
0.0		67.5	58.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0		-	56.9	0.41	0.22	0.07	0.99	0.31	-	tr.	-	-	tr.	-
2.0		65.1	57.0	0.74	0.32	0.12	1.46	0.37	0.20	0.03	0.04	0.00	0.07	0.00
3.1		-	54.2	0.95	0.37	0.18	2.05	0.47	-	0.06	0.05	-	0.12	-
5.0		58.7	52.8	1.99	0.61	0.28	3.39	0.61	0.55	0.06	0.09	0.00	0.17	0.00
6.0		-	50.0	2.42	0.71	0.33	4.03	0.65	-	0.09	0.10	-	0.18	-
8.0		50.3	47.9	3.80	1.15	0.58	5.77	0.81	0.98	0.17	0.18	0.04	0.33	tr.
9.5		-	45.2	4.88	1.37	0.66	6.28	0.97	-	0.20	-	-	-	-
11.0		39.4	41.4	7.87	2.18	1.15	8.59	1.41	1.09	0.24	0.31	-	0.55	0.21
14.3		-	34.0	14.7	3.84	1.94	13.0	1.97	-	-	-	-	-	-
16.0		6.11	28.1	30.3	7.45	3.47	19.7	2.48	1.34	0.60	0.70	0.16	1.10	0.45

TABLE NO. C. 12a (figs. C. 12., C. 27c, d.)

DATION NO. 12. Other Products

Time (min.)	HCHO (mm.)	CO (mm.)	Time (min.)	H_2O (mm.)	Time (min.)	H_2O (mm.)
1.3	0.91		0.6	0.78	9.0	7.70
1.3	0.88		1.3	1.06	9.6	8.46
2.7	1.62		1.3	1.39	10.3	11.0
2.7	1.28		1.3	0.91	11.6	13.5
2.7	1.51	0.65	1.9	1.13	11.6	14.8
4.0	1.51		1.9	0.99	12.9	17.4
4.0	2.03		2.6	1.06	12.9	19.0
4.0	1.84		3.2	1.44	14.1	31.1
5.3	2.74		3.9	1.59	14.1	24.3
5.3	2.15		4.5	2.22	14.8	26.9
6.7	2.69	2.13	5.1	1.69	15.4	29.4
8.0	4.24		5.1	2.92	15.4	30.8
8.0	3.43		6.4	2.76	17.4	28.4
8.0	3.82		6.8	3.09	18.0	29.1
8.0	3.72		7.7	3.80	19.3	31.6
10.7	5.25	5.78				
12.0	6.47					
16.0	10.7					
20.0	11.2					

Material Balance:

Time (min)	C	H	O
0	232	464	135
1.0	238	467	-
2.0	233	473	135
3.1	230	468	-
5.0	226	463	130
6.0	234	450	-
8.0	231	460	125
9.5	227	453	-
11.0	225	454	123

PRODUCT-TIME CURVES.

OXIDATION No. 12

Surface : Pyrex
isoButene : Oxygen = 1:1
Total Pressure = 120mm.
Temperature = 352°

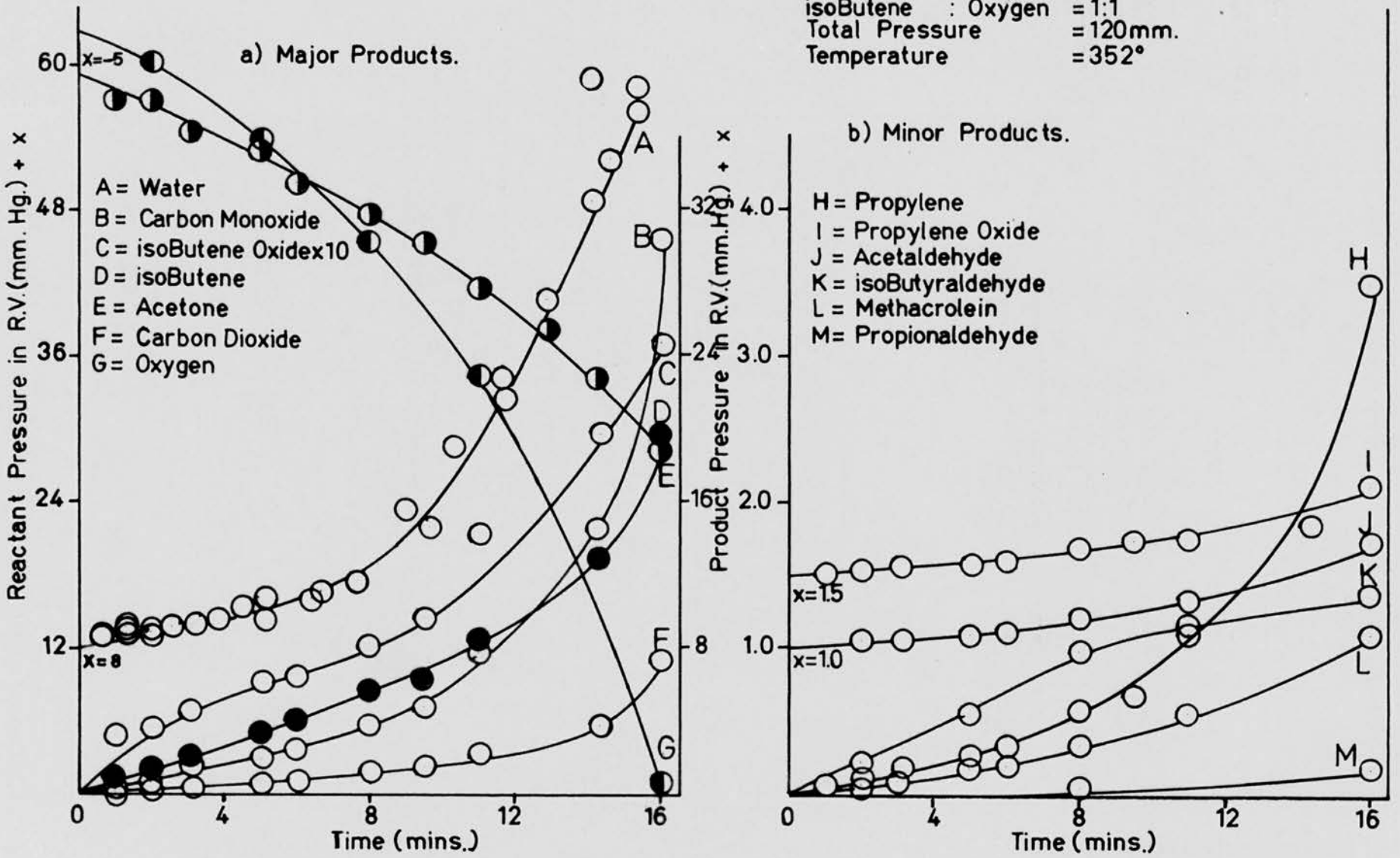


Figure C.12.

TABLE No.C.13 (fig.C.13)

OXIDATION No.13

Ratio $iC_4H_8 : O_2$ = 1 : 1 Total Pressure = 300 mm.Hg. Temperature = 246^0

Pressure in Reaction Vessel (mm.Hg.)

Time (min)	ΔP mm Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA
0	0.00	156.0	150.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	156.0	149.9	0.00	0.00	0.00	0.58	0.15	0.00	0.00	0.00	0.00
6	-0.05	157.3	150.0	0.14	0.02	0.00	1.42	0.33	0.00	0.00	0.00	0.00
9	-0.20	155.8	146.5	0.29	0.10	0.00	2.74	0.65	tr.	0.00	0.00	tr.
12	-0.40	149.7	145.8	0.53	0.19	0.02	4.12	0.95	tr.	tr.	tr.	-
18	-0.90	147.5	140.6	1.46	0.55	0.06	7.66	1.87	0.05	0.04	tr.	0.17
24	-1.29	136.0	136.2	3.05	1.10	0.15	11.6	2.64	0.06	0.07	0.05	0.19
30	-1.34	123.7	128.1	5.29	1.89	0.20	15.8	3.70	0.24	0.14	0.12	0.49
45	-1.27	100.8	113.2	-	4.56	0.36	25.4	6.14	0.45	0.20	0.19	0.69
60	+0.42	91.3	-	27.3	8.23	0.55	38.2	9.01	0.70	0.33	0.45	0.97
75	1.95	-	-	-	-	-	45.7	10.4	0.91	0.37	0.53	1.14

Material Balance

Time (min)	C	H	O
0	600	1200	312
3	603	1206	313
6	606	1213	319
9	600	1196	317
12	605	1210	309
18	603	1205	315
24	608	1204	306
30	600	1196	296

TABLE NO. C. 13a. (figs. C. 13., C. 24c, d.)

OXIDATION NO. 13.

Time (min.)	HCHO (mm.)	CO (mm.)
2	0.51	
3	0.71	
3	0.54	
3	0.59	0.11
3	0.59	
4	0.68	
5	0.86	
5	1.15	0.18
6	1.07	
6	1.01	0.30
6	1.01	
7	1.17	
9	1.84	
9	1.40	
9	1.47	
9	1.64	0.55
10	1.59	
10	2.15	0.73
12	3.03	
15	4.84	
15	4.12	1.57
16	5.14	
20	7.25	
24	6.56	
25	6.78	
30	11.0	
45	18.8	

Time (min.)	H_2O (mm.)
4.5	0.56
7.5	0.82
10.5	1.89
13.5	1.04
18.0	2.45
22.5	4.75
24.0	4.62
36.0	8.85
40.5	11.8
48.0	17.9
51.0	18.3
54.0	22.4
63.0	27.9
67.0	31.8
72.0	34.6
75.0	40.3
81.0	44.8
87.0	53.7
90.0	48.1
94.0	55.0
99.0	61.0
104.0	56.0
108.0	60.5
112.0	62.0
117.0	62.6
121.0	60.0
127.0	65.5
132.0	62.0
135.0	64.0

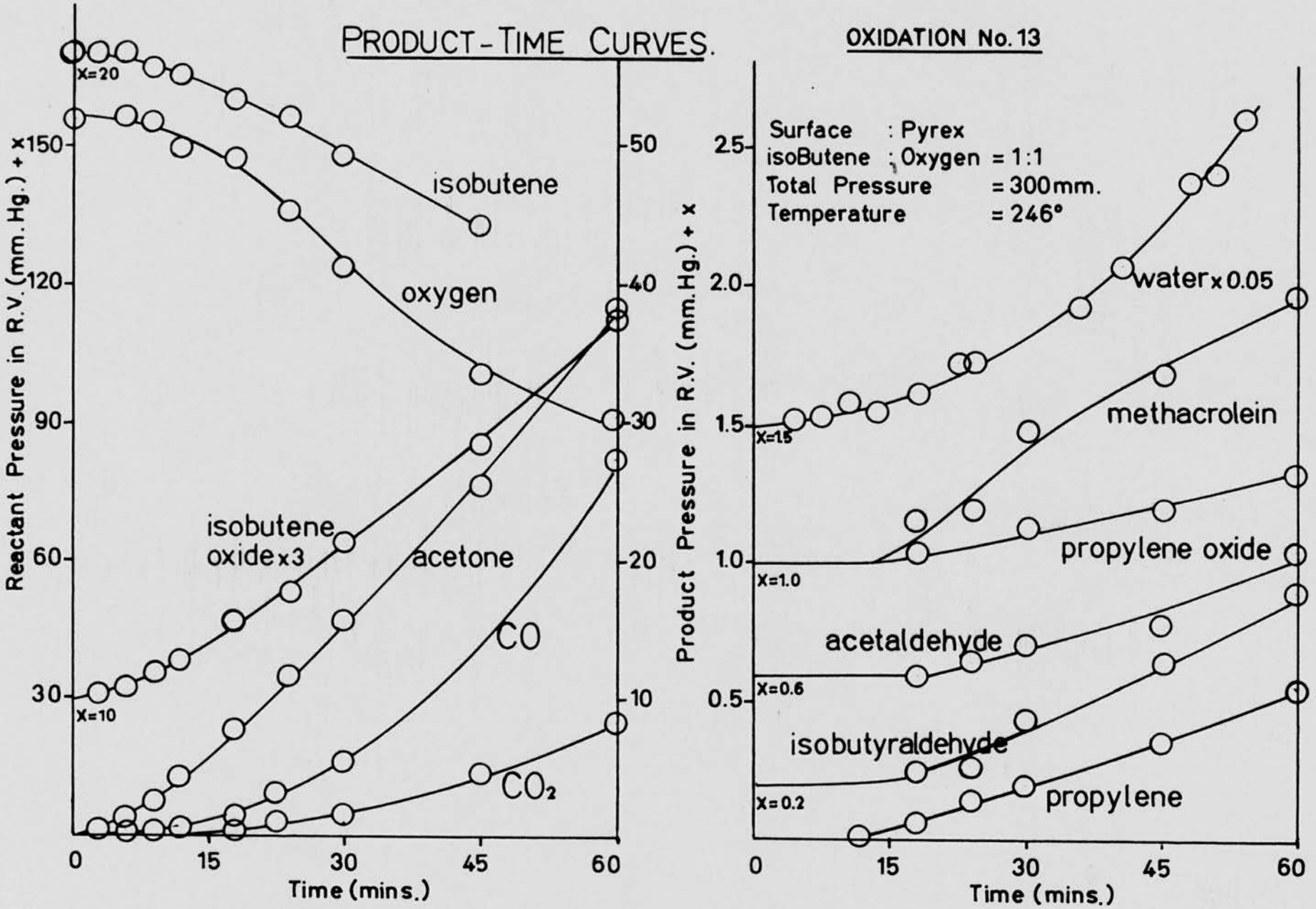

PRODUCT-TIME CURVES.
OXIDATION No. 13
Surface : Pyrex
isoButene : Oxygen = 1:1
Total Pressure = 300mm.
Temperature = 246°
Reactant Pressure in R.V. (mm.Hg.) + x
Product Pressure in R.V. (mm.Hg.) + x
Time (mins.)
isobutene
oxygen
isobutene oxide x3
acetone
CO
CO2
water x 0.05
methacrolein
propylene oxide
acetaldehyde
isobutyraldehyde
propylene
X=20
X=10
X=1.5
X=1.0
X=0.6
X=0.2

Figure C. 13.

2.3 The effect of surface and inert gas

The effect on the oxidation of varying the nature of the surface of the reaction vessel was studied by coating the surface with various inorganic compounds and conditioning the vessel as previously described. Three runs were then carried out with each of the following surfaces to assess any variation in the results due to activation or deterioration of the surface film.

(a) Boric acid (Oxidation Nos. 14 - 16)

(b) Potassium chloride (" Nos. 17 -19)

(c) Sodium hydroxide (" Nos. 20 - 22)

After the third run in the sodium hydroxide coated vessel, a further run (Oxidation No. 23) was carried out in which the reaction mixture contained an excess of nitrogen.

TABLE Nos.C.14., C.15., C.16 (figs.C.14., C.15., C.16., C.29a)

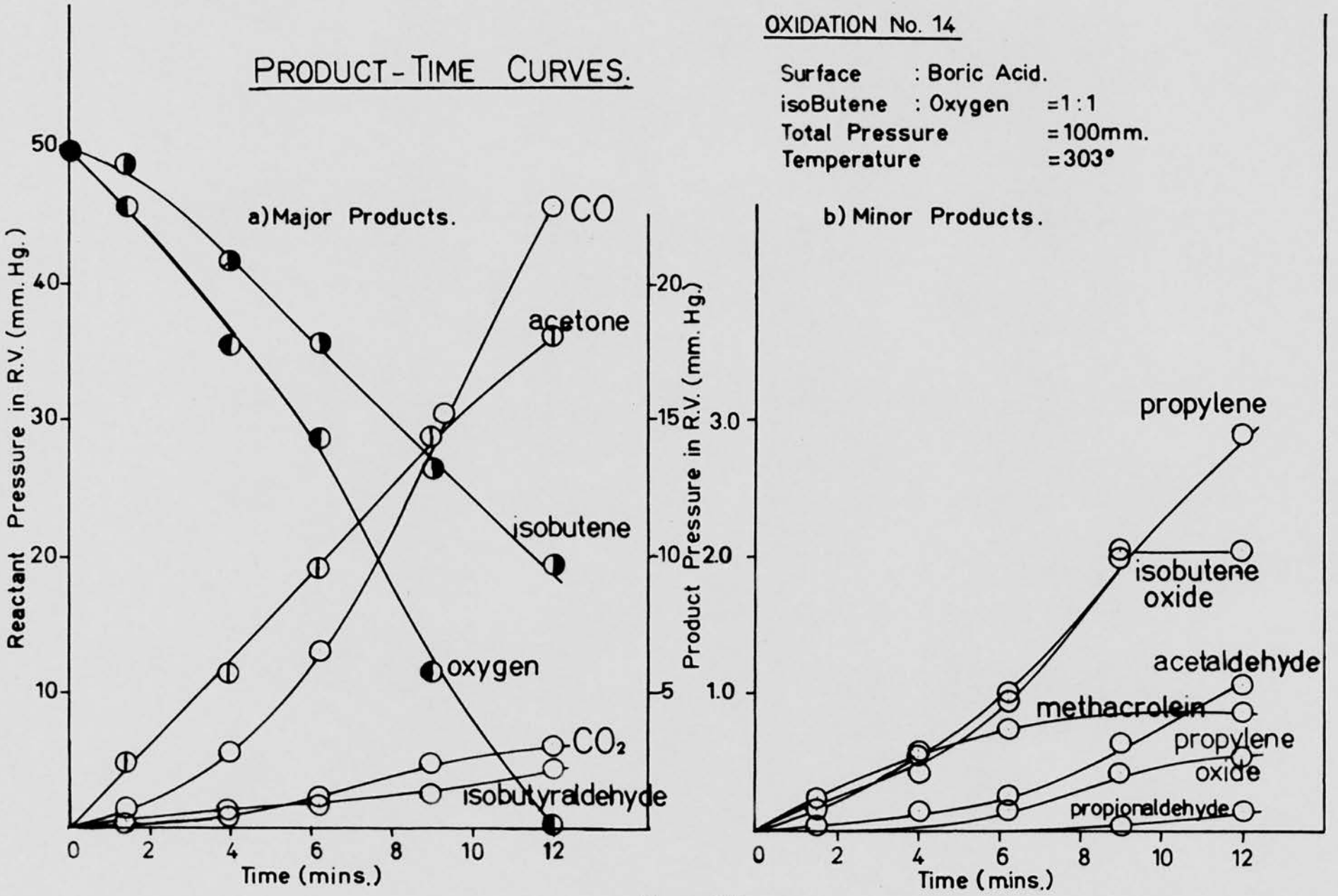
OXIDATION No.14 = 100 mm.Hg.
OXIDATION No.15 = 85 mm.Hg.
OXIDATION No.16 = 100 mm.Hg. Ratio $iC_4H_8 : O_2$ = 1:1 Temperature = 303°

Pressure in Reaction Vessel (mm.Hg.)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	C_2H_5CHO	MA	CH_4	HCHO
Ox. No.14															
0.0	0.00	49.5	49.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-
1.5	-0.11	45.6	48.6	0.78	0.25	0.15	2.30	0.22	0.41	tr.	tr.	0.00	-	0.00	-
4.0	+0.11	35.4	41.7	2.79	0.50	0.54	5.62	0.42	0.68	-	0.14	tr.	0.58	0.00	-
6.25	0.86	28.5	35.4	6.50	1.18	1.02	9.50	0.96	0.93	0.17	0.26	tr.	0.73	0.00	-
9.0	2.98	11.6	26.4	15.2	2.40	2.00	14.4	2.08	1.33	0.41	0.63	0.05	0.53	0.00	-
12.0	5.41	0.31	19.1	22.8	3.07	2.90	18.1	2.08	2.15	0.54	1.08	0.14	0.89	0.70	-
Ox. No.15															
0.0	0.00	44.2	41.3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-
2.5	-0.15	39.0	36.6	0.91	0.18	0.16	-	-	-	-	-	-	-	-	-
5.5	+0.52	29.1	30.9	3.74	0.66	0.62	7.93	0.23	1.33	0.20	0.32	tr.	0.56	0.00	-
9.0	+4.05	6.70	18.0	14.3	2.04	1.72	17.4	1.11	1.61	0.34	0.96	0.15	0.62	0.17	-
12.0	5.37	0.86	16.1	18.8	2.48	2.04	19.7	1.43	2.38	0.56	1.13	0.21	0.72	0.61	-
Ox. No.16															
0.0	0.00	51.5	48.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2.5	-0.16	45.2	46.4	1.52	0.29	0.24	3.14	0.00	0.51	0.07	0.09	-	-	0.00	-
5.5	+0.64	33.2	36.7	5.08	0.86	0.78	7.32	0.00	1.18	0.11	0.21	0.07	0.35	0.00	-
9.0	5.46	6.39	24.2	23.3	3.33	2.69	18.0	0.87	1.76	0.36	1.18	-	0.74	0.33	-
11.5	6.71	0.13	19.6	29.3	3.90	3.00	20.4	1.39	2.34	0.56	1.20	0.13	0.68	1.29	-
14.0	6.78	0.11	-	28.6	-	-	20.4	0.75	2.97	0.52	1.26	0.19	1.09	1.28	-

(Cont'd)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	C_2H_5CHO	MA	CH_4	HCHO
1.0	-	-	-	-	-	-	2.55	-	-	-	-	-	-	-	2.14
3.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.50
7.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8.05
7.0	-	-	-	-	-	-	12.4	-	-	-	-	-	-	-	9.45
9.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	11.3
18.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	19.7


PRODUCT-TIME CURVES.
OXIDATION No. 14
Surface : Boric Acid.
isoButene : Oxygen =1:1
Total Pressure =100mm.
Temperature =303°
a) Major Products.
b) Minor Products.
Reactant Pressure in R.V. (mm. Hg.)
Product Pressure in R.V. (mm. Hg.)
Time (mins.)
CO
acetone
isobutene
oxygen
CO2
isobutyraldehyde
propylene
isobutene oxide
acetaldehyde
methacrolein
propylene oxide
propionaldehyde

FigureC14.

PRODUCT-TIME CURVES.

OXIDATION No. 15

Surface : Boric Acid.
isoButene : Oxygen =1:1
Total Pressure = 85mm.
Temperature =303°

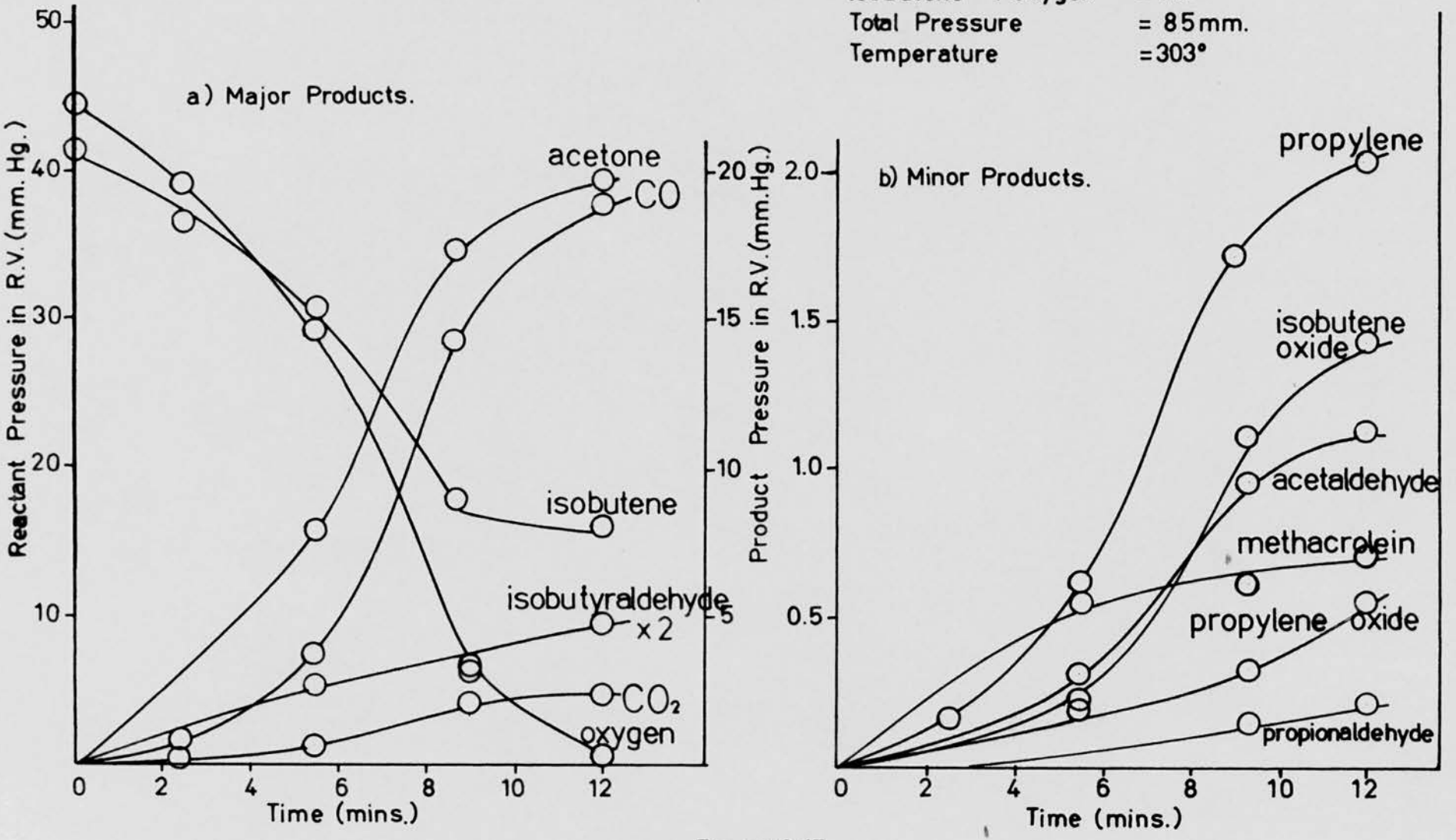
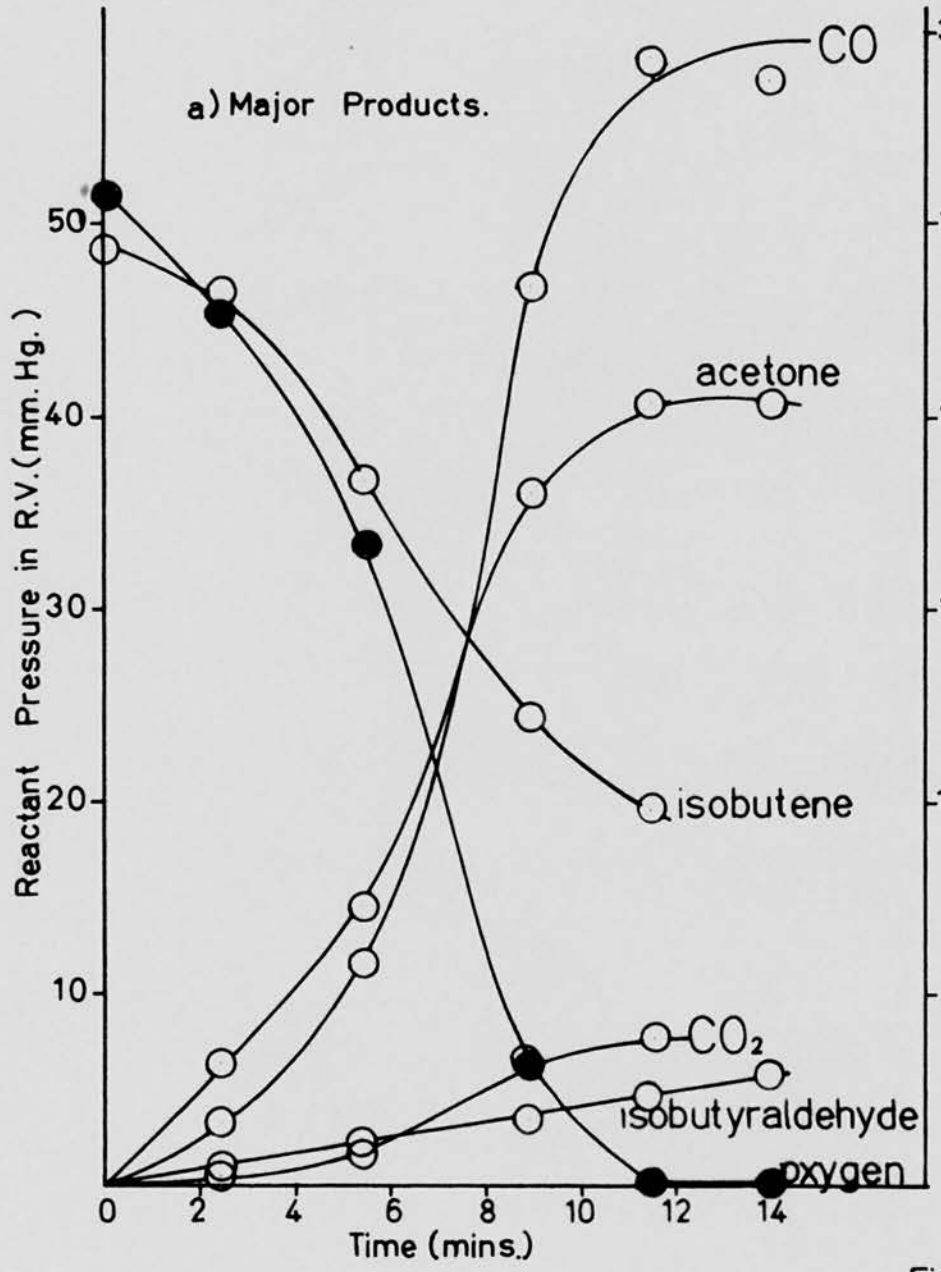


Figure C.15.

OXIDATION No. 16

PRODUCT-TIME CURVES.

Surface : Boric Acid.
isoButene : Oxygen = 1 : 1
Total Pressure = 100mm.
Temperature = 303°



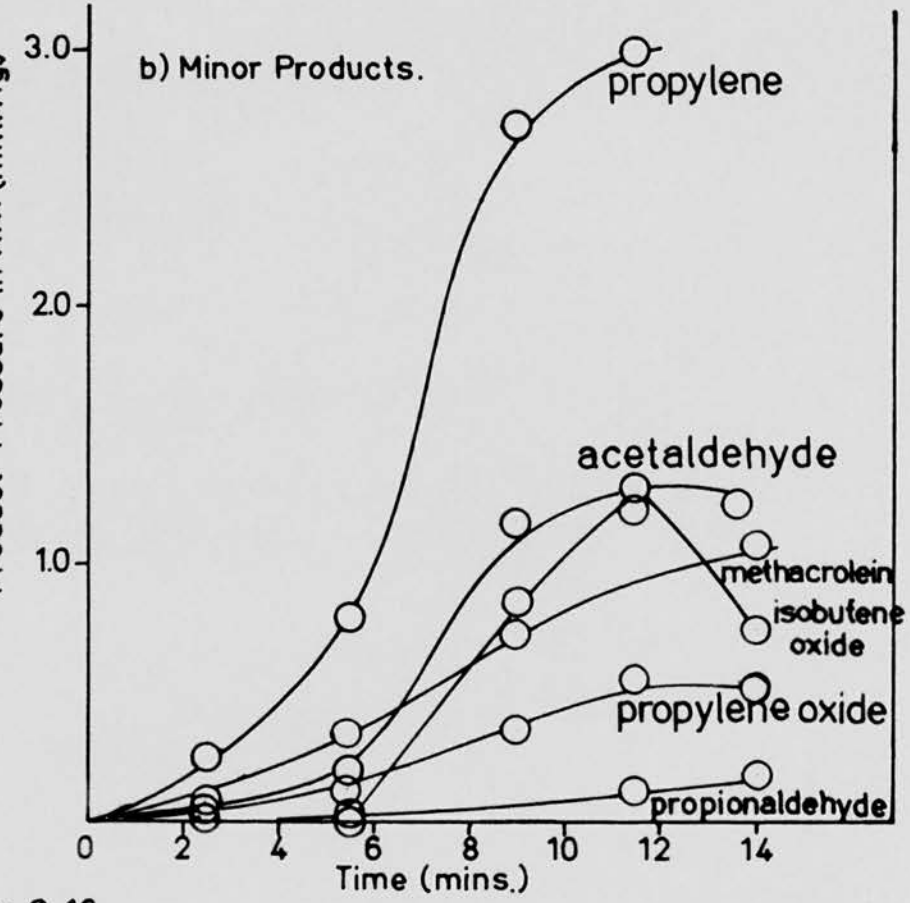


Figure C. 16.

TABLE Nos. C.17., C.18., C.19. (figs.C.17., C.18., C.19., C.29.b)

OXIDATION No.17. = 215 mm.Hg,
OXIDATION No.18. = 215 mm.Hg.
OXIDATION No.19. = 215 mm.Hg.

Ratio $iC_4H_8 : O_2$ = 1:1 Temperature = 303°

Pressure in Reaction Vessel (mm.Hg.)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	C_2H_5CHO	MA	CH_4	HCHO
Ox.No.17															
0	0.00	107.0	107.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-
2	-0.11	92.5	93.7	5.72	-	0.54	12.5	3.46	0.06	0.31	0.08	0.00	0.39	0.00	-
4	+0.49	79.4	85.7	10.4	3.73	0.85	17.7	5.00	0.22	0.45	0.24	0.00	0.79	0.00	-
6	1.16	71.8	75.0	14.1	5.41	0.96	22.4	6.24	0.41	0.68	0.27	0.00	1.20	0.00	-
8	1.92	65.5	71.2	17.6	7.01	1.10	25.4	7.58	0.37	0.70	0.28	tr.	0.83	tr.	-
10	2.60	56.5	67.1	20.8	7.35	1.20	27.9	8.81	0.37	0.67	0.26	-	1.13	0.12	-
Ox.No.18															
0	0.00	107.2	107.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-
4	+0.89	79.2	80.4	9.70	3.88	0.81	19.2	5.58	0.22	0.48	0.18	0.00	0.84	0.00	-
8	2.88	58.2	68.3	17.8	7.50	1.14	27.8	8.58	0.25	0.82	0.31	0.00	1.03	0.00	-
12	4.87	41.1	62.0	26.0	11.6	1.39	33.6	10.6	0.29	0.95	0.52	0.00	1.38	tr.	-
16	6.54	30.2	57.6	32.2	14.7	1.59	39.3	12.6	0.38	1.20	0.50	0.00	1.37	0.16	-
20	7.99	20.7	53.6	40.0	16.5	1.65	41.5	12.5	1.43	1.23	0.65	tr.	1.33	0.19	
Ox.No.19															
0	0.00	108.2	108.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	+0.05	95.6	88.9	5.15	2.29	0.51	11.3	3.11	0.33	0.50	0.16	tr.	0.36	-	-
5	1.13	77.0	79.0	10.8	4.73	0.86	18.5	5.59	0.25	0.42	0.23	tr.	1.03	-	-
8	2.26	63.7	72.9	16.8	6.89	1.08	24.1	7.33	0.24	0.68	0.26	0.16	1.15	-	-
11	3.43	51.9	66.7	21.9	9.88	1.24	27.7	9.20	0.19	0.86	0.35	0.14	1.10	-	-
15	4.89	40.9	61.7	27.3	12.3	1.42	32.6	10.6	0.20	0.86	0.39	0.10	1.28	-	-
2	-	-	-	-	-	-	8.46	-	-	-	-	-	-	-	6.53

Cont.)

Time (min)	ΔP mm. Hg.	0_2	iC_4H_8	C0	$C0_2$	C_3H_6	Me_2C0	iC_4H_80	iC_3H_7CH0	C_3H_60	CH_3CH0	C_2H_5CH0	MA	CH_4	HCH0
3	-	-	-	-	-	-	9.42	-	-	-	-	-	-	-	6.86
4	-	-	-	-	-	-	11.4	-	-	-	-	-	-	-	7.95
5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9.01
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9.30
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	11.8

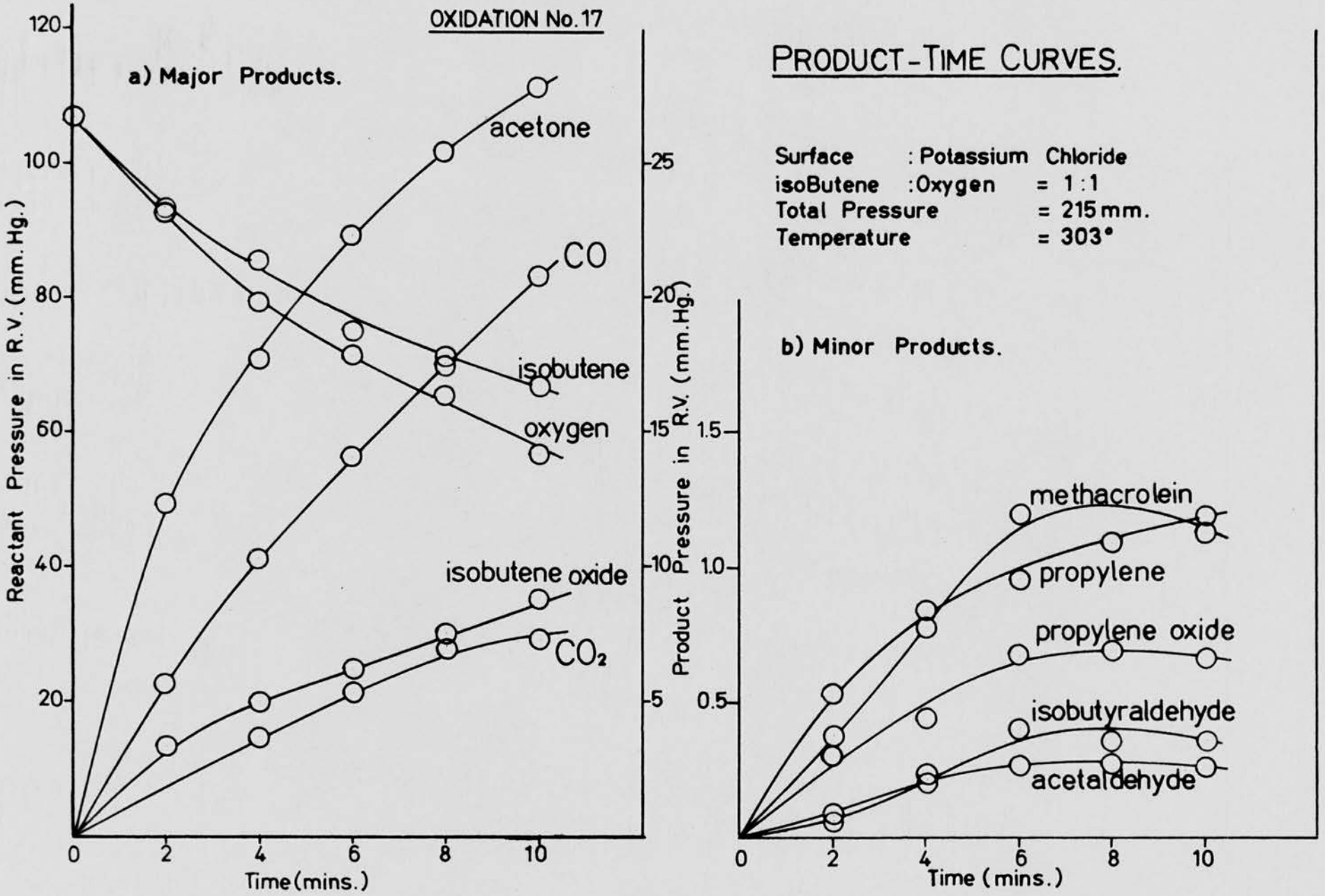

OXIDATION No. 17
a) Major Products.
PRODUCT-TIME CURVES.
Surface : Potassium Chloride
isoButene : Oxygen = 1 : 1
Total Pressure = 215 mm.
Temperature = 303°
Reactant Pressure in R.V. (mm. Hg.)
Product Pressure in R.V. (mm. Hg.)
Time (mins.)
acetone
CO
isobutene
oxygen
isobutene oxide
CO2
b) Minor Products.
methacrolein
propylene
propylene oxide
isobutyraldehyde
acetaldehyde

Figure C. 17.

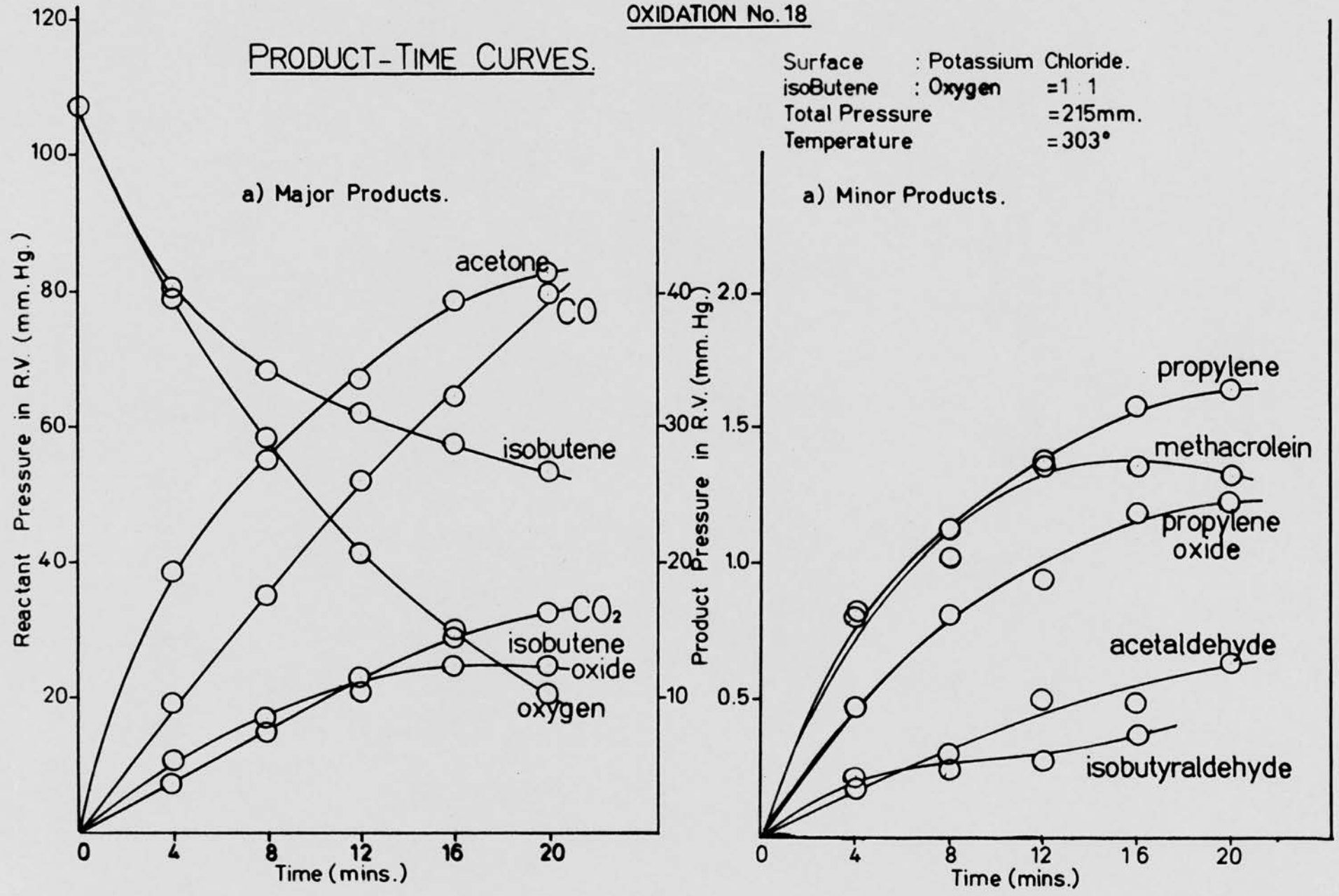

OXIDATION No. 18
PRODUCT-TIME CURVES.
Surface : Potassium Chloride.
isoButene : Oxygen =1 : 1
Total Pressure =215mm.
Temperature =303°
a) Major Products.
a) Minor Products.
Reactant Pressure in R.V. (mm.Hg.)
Product Pressure in R.V. (mm.Hg.)
acetone
CO
isobutene
CO_2
isobutene oxide
oxygen
propylene
methacrolein
propylene oxide
acetaldehyde
isobutyraldehyde
Time (mins.)
Time (mins.)

Figure C. 18.

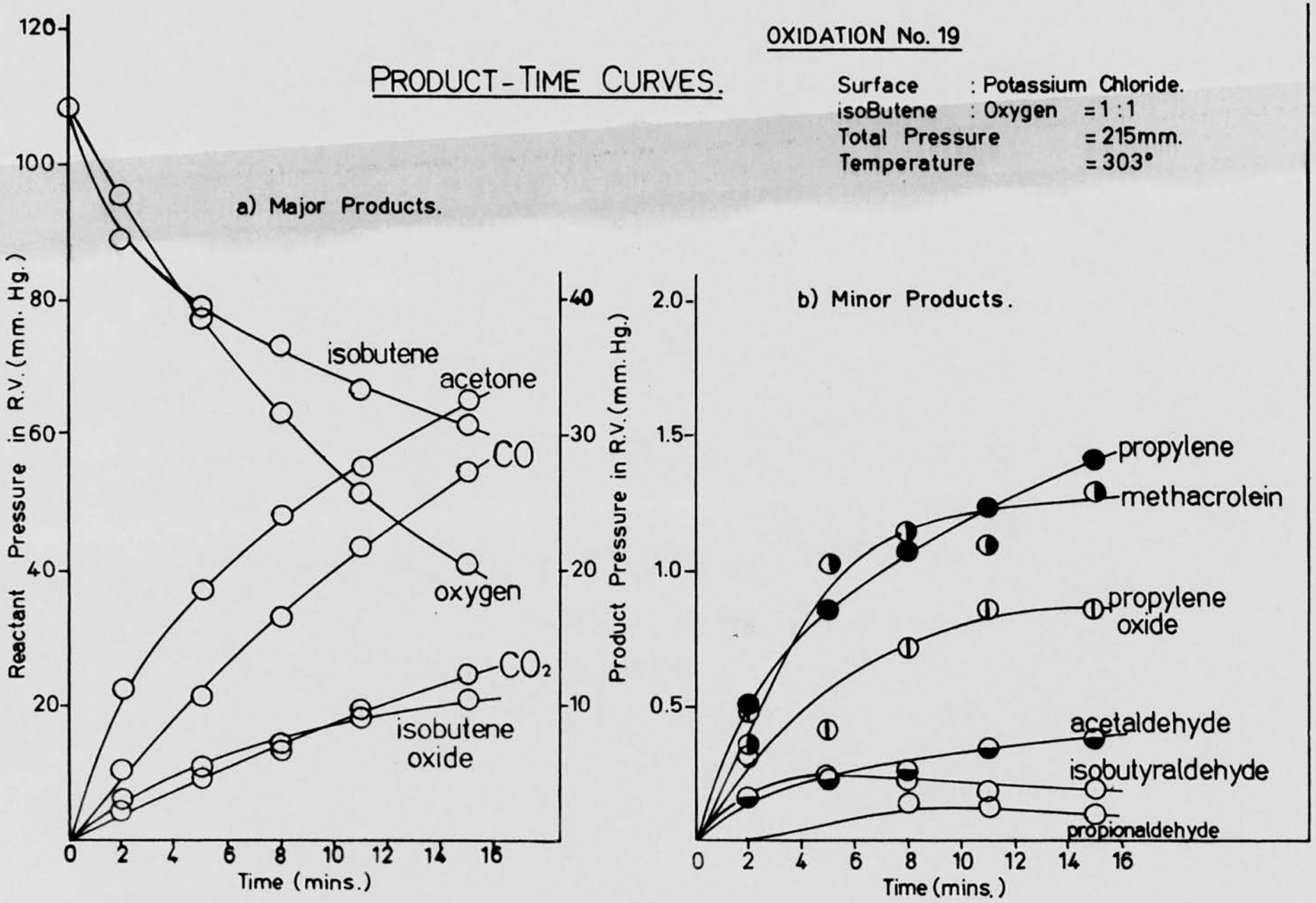

PRODUCT-TIME CURVES.
OXIDATION No. 19
Surface : Potassium Chloride.
isoButene : Oxygen = 1 : 1
Total Pressure = 215mm.
Temperature = 303°
a) Major Products.
Reactant Pressure in R.V. (mm. Hg.)
Product Pressure in R.V. (mm. Hg.)
isobutene
acetone
CO
oxygen
CO_2
isobutene oxide
Time (mins.)
b) Minor Products.
propylene
methacrolein
propylene oxide
acetaldehyde
isobutyraldehyde
propionaldehyde
Time (mins.)

Figure C.19.

TABLE Nos.C.20., C.21., C.22. (figs.C.20., C.21., C.22., C.29c)

OXIDATION No.20 = 215 mm.Hg.
OXIDATION No.21 = 215 mm.Hg.
OXIDATION No.22 = 215 mm.Hg.

Ratio $iC_4H_8 : O_2$ = 1:1 Temperature = 303°

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	C_2H_5CHO	MA	CH_4	HCHO
Ox.No.20.															
0	0.00	107.3	107.3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0,00	-
5	+0.27	85.9	88.2	6.62	6.53	0.58	13.9	3.99	0.19	0.35	0.17	tr.	0.52	0.00	-
10	2.80	54.2	70.6	17.1	14.2	1.12	24.7	8.09	0.21	0.48	0.56	tr.	1.05	tr.	-
15	5.08	30.3	64.3	27.6	20.7	1.58	31.1	10.7	0.25	0.84	0.40	tr.	0.97	0.07	-
20	6.49	16.0	58.7	34.0	25.0	1.84	36.0	12.8	0.26	1.16	0.86	0.10	1.04	0.07	-
25	7.27	7.64	55.6	37.4	29.1	1.85	39.9	13.8	0.28	1.29	1.08	0.12	1.04	0.30	-
Ox. No.21															
0	0.00	108.0	108.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-
3	+0.10	85.6	80.6	4.56	5.72	0.45	10.4	2.89	0.06	0.25	0.09	tr.	0.88	tr.	-
6	1.05	68.1	65.2	10.4	8.43	0.79	18.3	5.56	0.07	0.44	0.25	tr.	0.81	0.10	-
9	2.39	47.6	58.8	16.2	12.4	1.05	24.5	7.69	0.13	0.72	0.44	tr.	0.74	-	-
12	3.69	35.1	58.1	22.2	16.3	1.33	30.6	10.2	0.20	0.93	0.68	0.05	1.10	0.17	-
15	4.70	25.2	50.9	25.3	18.0	1.29	33.0	11.2	0.18	1.03	0.63	0.09	1.22	0.24	-
Ox. No.22															
0	0.00	107.4	107.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	+0.79	73.8	77.2	6.43	7.83	0.58	12.6	3.82	0.20	0.34	0.12	0.08	0.70	tr.	-
8	2.49	51.6	62.9	14.9	12.6	0.98	22.8	7.26	0.22	0.52	0.37	0.10	0.56	0.18	-
12	4.24	31.2	54.4	23.1	17.0	1.27	28.6	9.34	0.18	0.78	0.51	-	0.84	0.29	

Ex. No. 22
(Con'd)

Time (min)	ΔP mm. Hg.	0_2	iC_4H_8	C0	$C0_2$	C_3H_6	Me_2C0	iC_4H_8 0	iC_3H_7 CH0	C_3H_6 0	CH_3 CH0	C_2H_5 CH0	MA	CH_4	HCHO
16	5.78	18.1	51.2	32.1	20.5	1.43	34.4	11.4	0.16	1.02	0.68	0.12	0.83	0.31	-
20	6.77	10.3	43.4	33.3	20.5	1.47	37.4	12.8	0.43	1.03	0.92	0.11	1.15	0.70	-
2	-	-	-	-	-	-	7.00	-	-	-	-	-	-	-	3.80
5	-	-	-	-	-	-	17.5	-	-	-	-	-	-	-	6.90
8	-	-	-	-	-	-	21.5	-	-	-	-	-	-	-	10.3

PRODUCT-TIME CURVES.

Surface : Sodium Hydroxide
isoButene : Oxygen = 1 : 1
Total Pressure = 215 mm.
Temperature = 303°

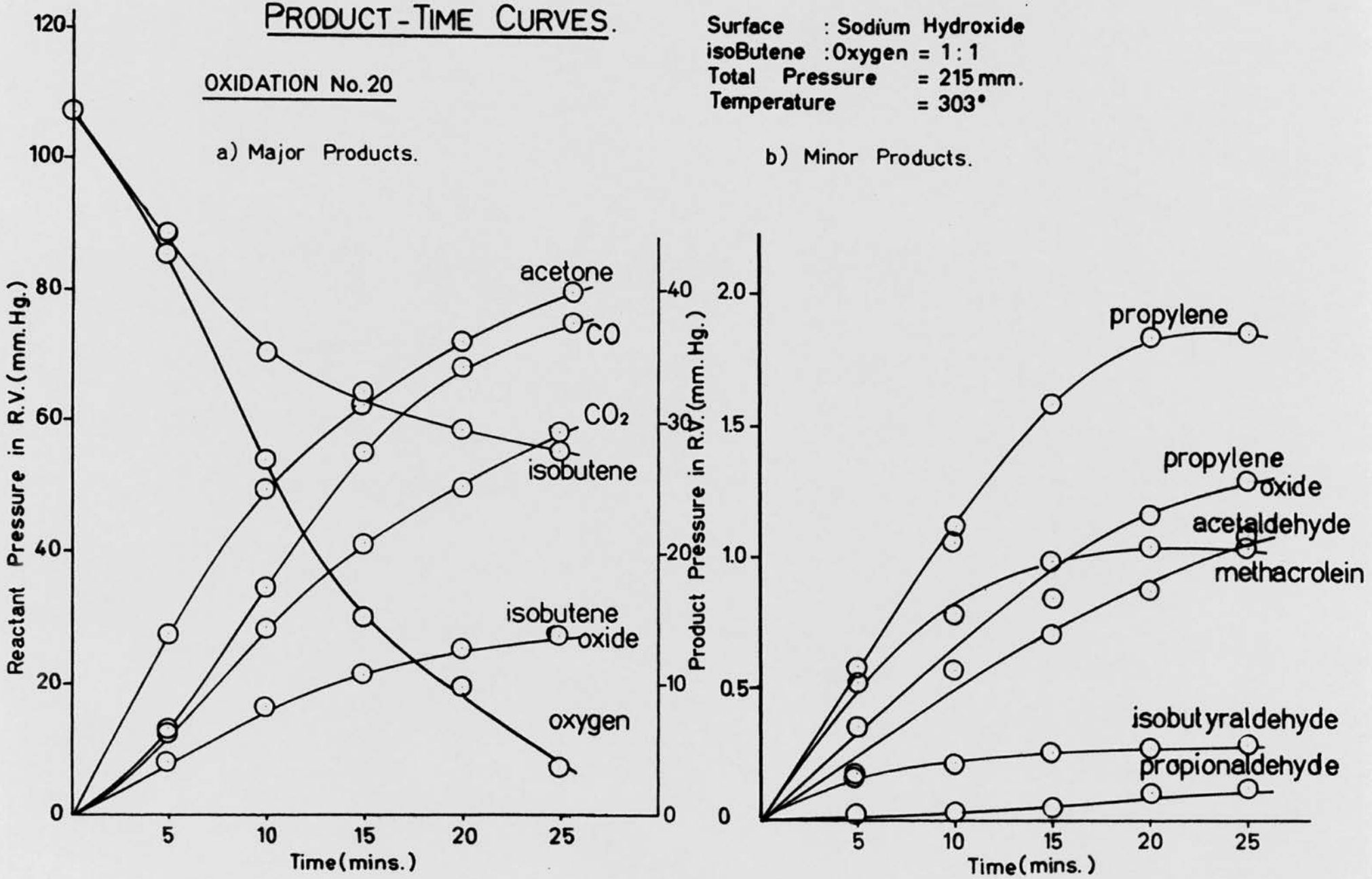


Figure C. 20.

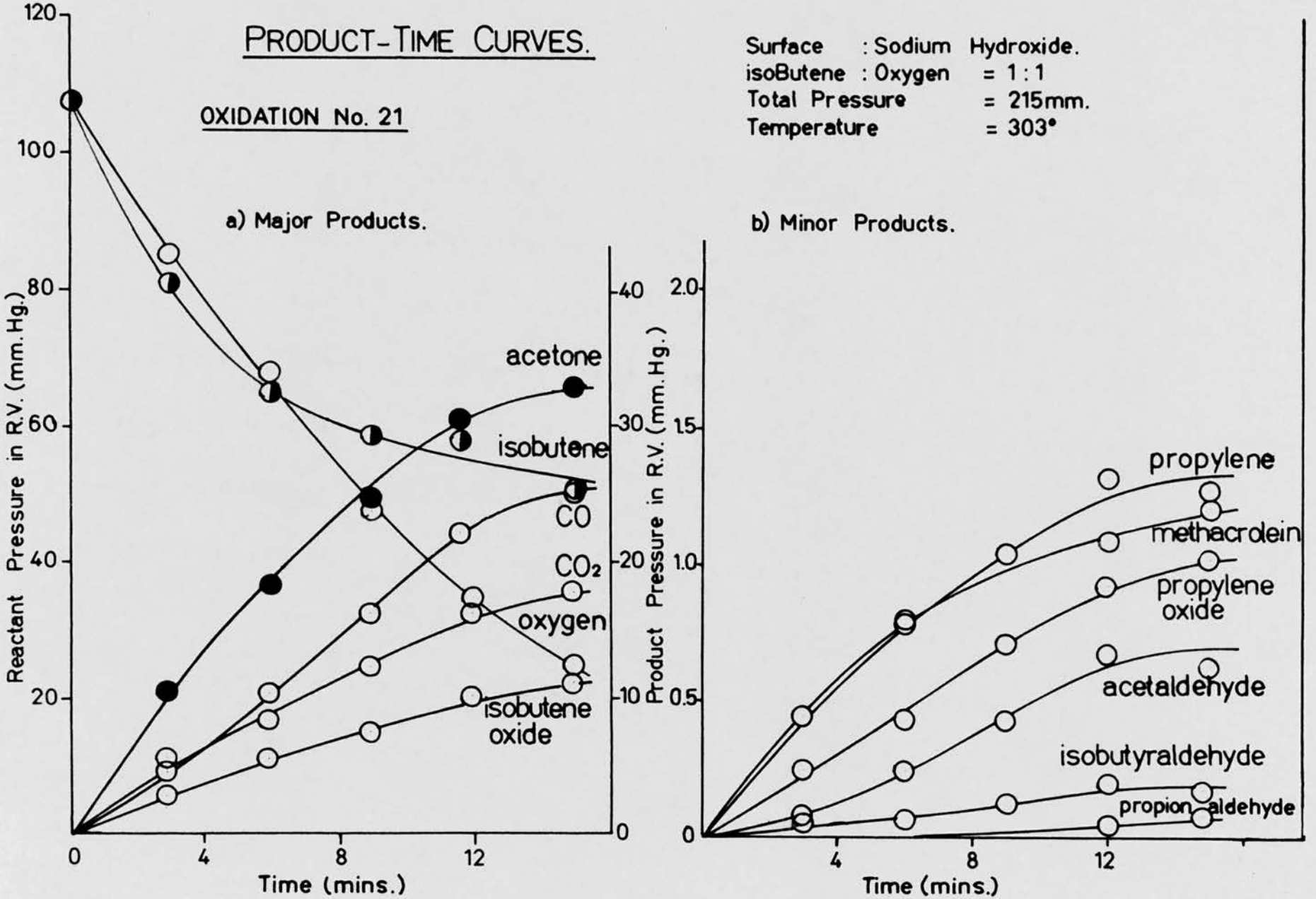

PRODUCT-TIME CURVES.
OXIDATION No. 21
Surface : Sodium Hydroxide.
isoButene : Oxygen = 1 : 1
Total Pressure = 215mm.
Temperature = 303°
a) Major Products.
b) Minor Products.
Reactant Pressure in R.V. (mm.Hg.)
Product Pressure in R.V. (mm.Hg.)
Time (mins.)
acetone
isobutene
CO
CO2
oxygen
isobutene oxide
propylene
methacrolein
propylene oxide
acetaldehyde
isobutyraldehyde
propion aldehyde

Figure C.21.

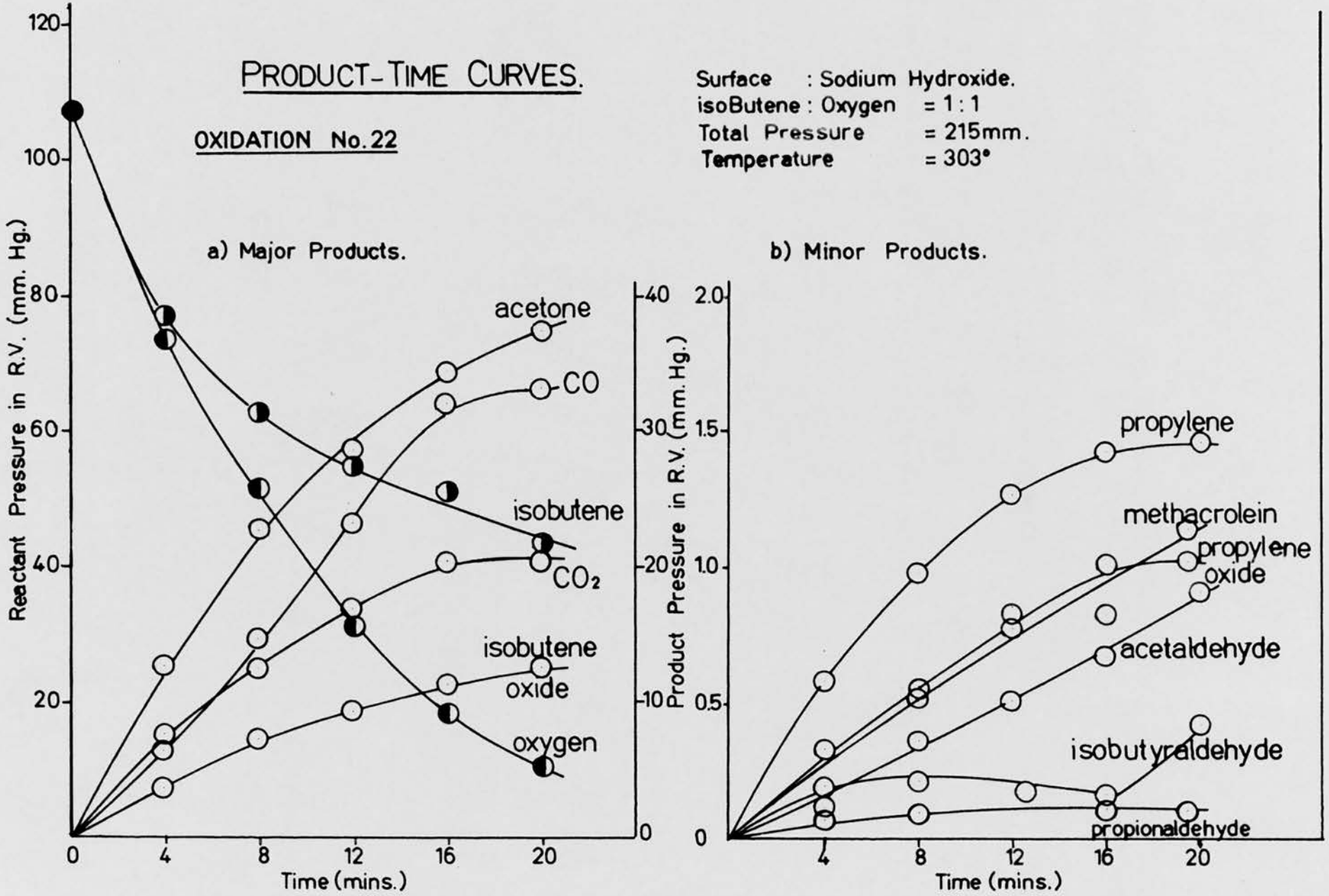

PRODUCT-TIME CURVES.
OXIDATION No. 22
Surface : Sodium Hydroxide.
isoButene : Oxygen = 1 : 1
Total Pressure = 215mm.
Temperature = 303°
a) Major Products.
b) Minor Products.
Reactant Pressure in R.V. (mm. Hg.)
Product Pressure in R.V. (mm. Hg.)
Time (mins.)
acetone
CO
isobutene
CO2
isobutene oxide
oxygen
propylene
methacrolein
propylene oxide
acetaldehyde
isobutyraldehyde
propionaldehyde

Figure C.22.

TABLE No.C23. (fig. C.23.)

OXIDATION No.23

Pressure Ratio $iC_4H_8 : O_2 : N_2$ = 90 : 90 : 205 Temperature = 303°

Pressure in Reaction Vessel (mm.Hg.)

Time (min)	ΔP mm. Hg.	O_2	iC_4H_8	CO	CO_2	C_3H_6	Me_2CO	iC_4H_8O	iC_3H_7CHO	C_3H_6O	CH_3CHO	MA
0	0.00	90.4	90.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	+0.21	77.4	80.5	2.56	5.41	0.31	7.06	1.81	0.12	0.20	0.08	0.24
4	0.48	69.2	70.8	4.80	7.72	0.43	11.1	2.92	0.16	0.30	0.11	0.41
6	0.82	55.4	65.6	7.22	9.10	0.62	14.2	3.86	-	0.33	0.15	0.48
9	1.49	43.6	59.8	10.4	10.9	0.78	18,4	5.15	0.17	0.48	0.30	0.65
12	2.09	34.6	53.8	13.6	13.2	0.87	21.4	6.37	0.15	0.54	0.26	0.70

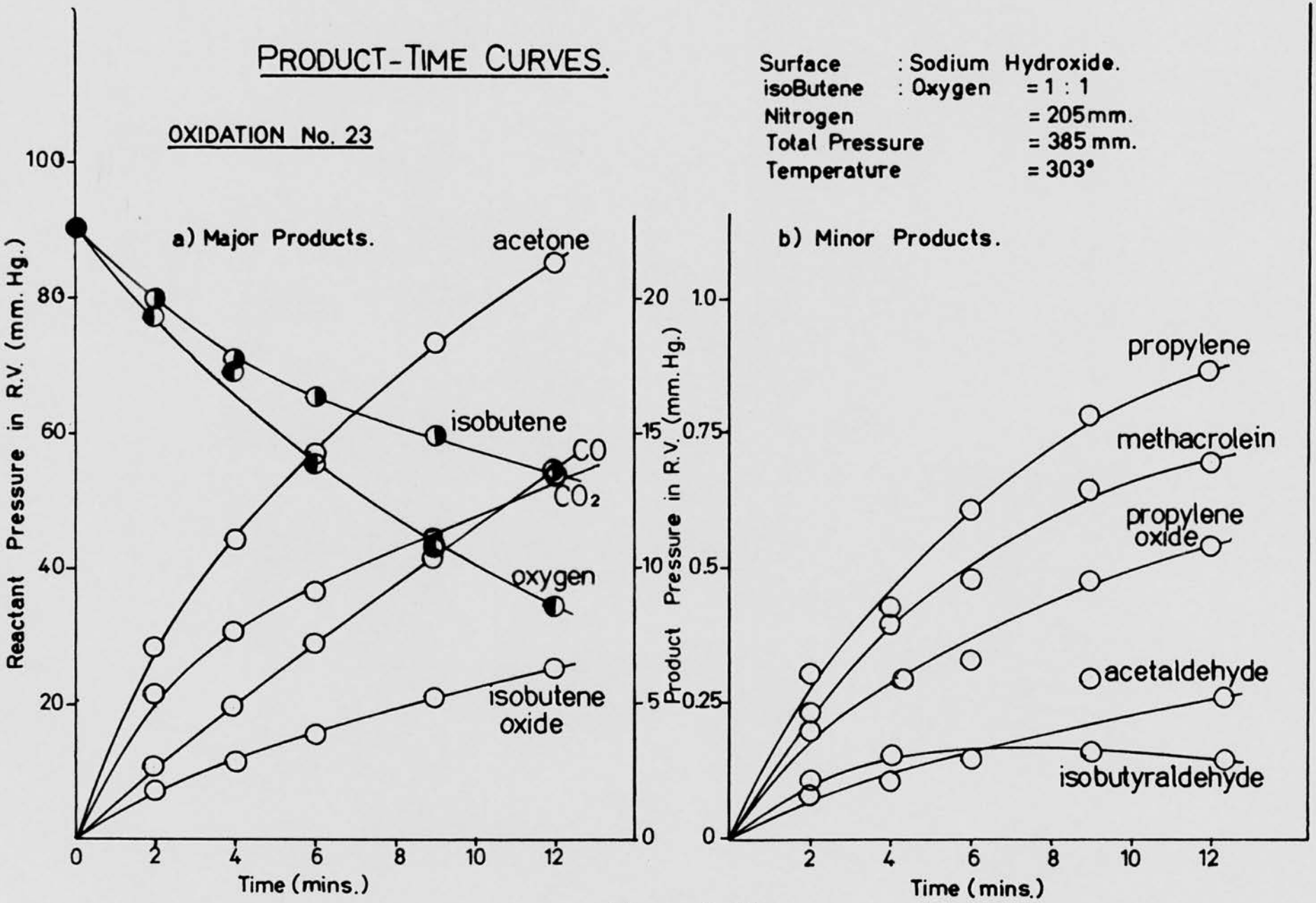

PRODUCT-TIME CURVES.
OXIDATION No. 23
Surface : Sodium Hydroxide.
isoButene : Oxygen = 1 : 1
Nitrogen = 205mm.
Total Pressure = 385 mm.
Temperature = 303°
a) Major Products.
b) Minor Products.
Reactant Pressure in R.V. (mm. Hg.)
Product Pressure in R.V. (mm. Hg.)
Time (mins.)
Time (mins.)
acetone
isobutene
CO
CO2
oxygen
isobutene oxide
propylene
methacrolein
propylene oxide
acetaldehyde
isobutyraldehyde

Figure C. 23.

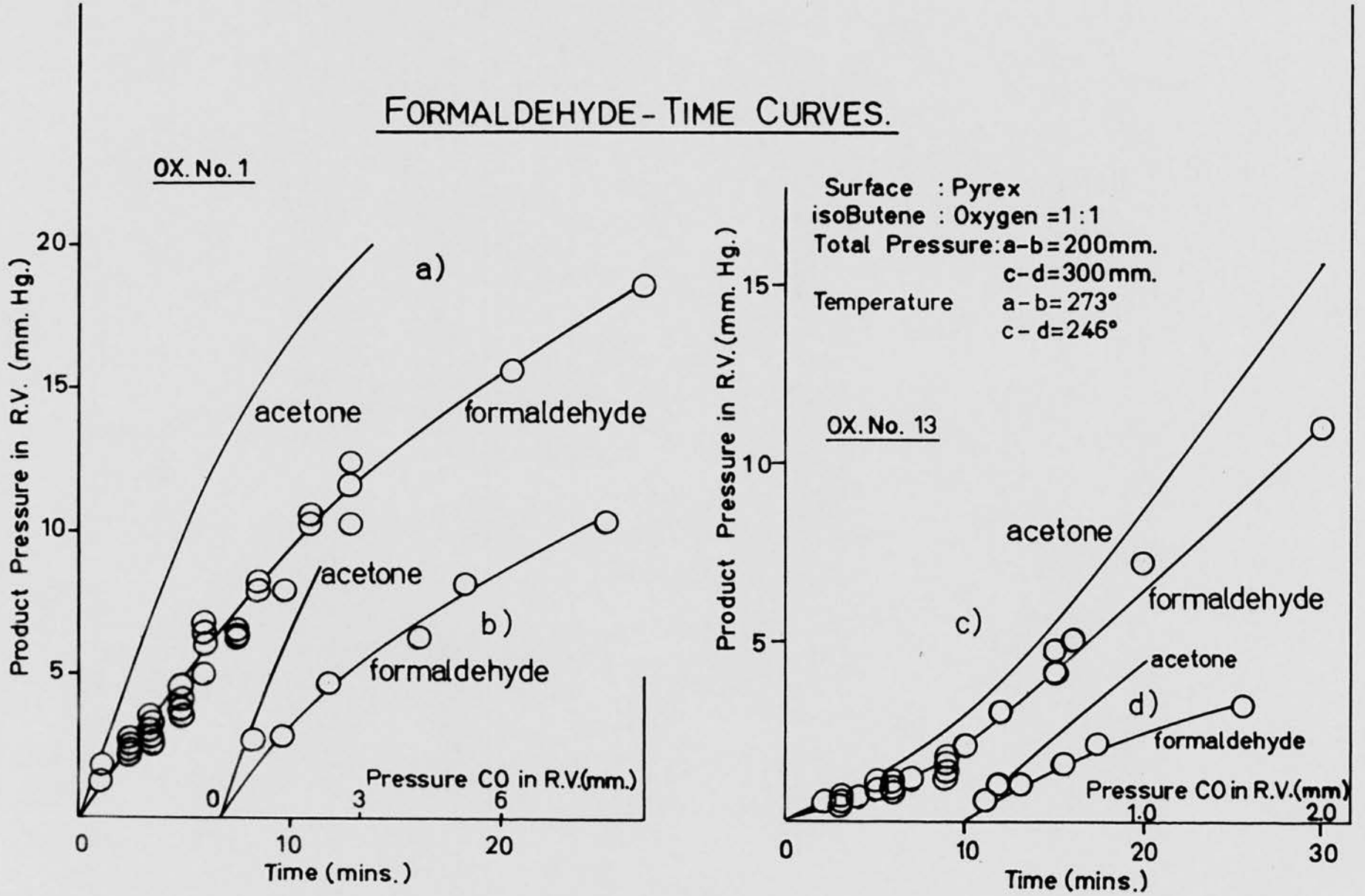

FORMALDEHYDE-TIME CURVES.
OX. No. 1
a)
acetone
formaldehyde
acetone
b)
formaldehyde
Product Pressure in R.V. (mm. Hg.)
Pressure CO in R.V.(mm.)
0
3
6
Time (mins.)
Surface : Pyrex
isoButene : Oxygen =1 : 1
Total Pressure: a-b=200mm.
c-d=300mm.
Temperature a-b=273°
c-d=246°
OX. No. 13
acetone
formaldehyde
c)
acetone
d)
formaldehyde
Product Pressure in R.V.(mm. Hg.)
Pressure CO in R.V.(mm)
1.0
2.0
Time (mins.)

Figure C.24.

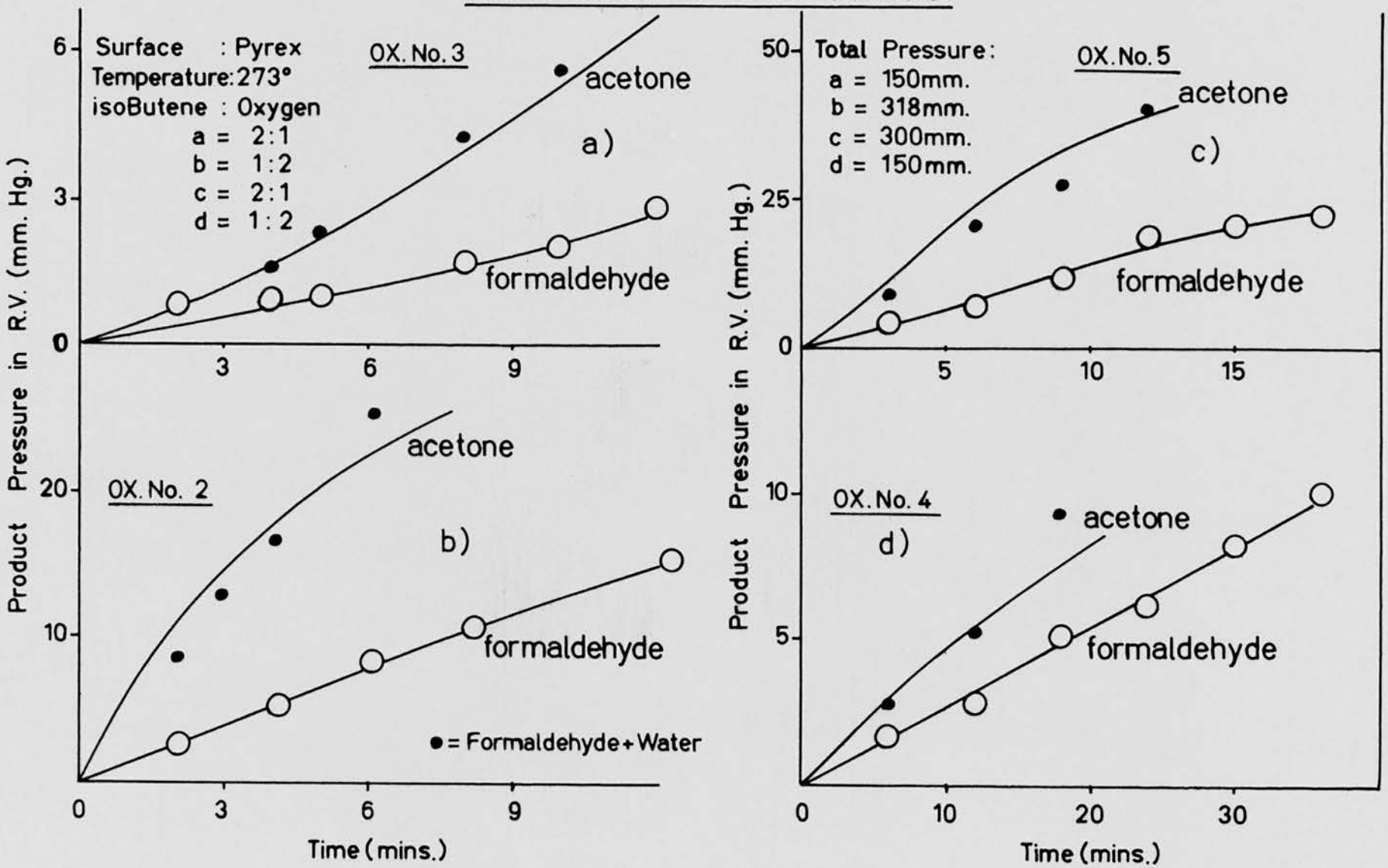

FORMALDEHYDE-TIME CURVES.
Surface : Pyrex
Temperature: 273°
isoButene : Oxygen
a = 2:1
b = 1:2
c = 2:1
d = 1:2
OX. No. 3
acetone
a)
formaldehyde
OX. No. 2
acetone
b)
formaldehyde
● = Formaldehyde + Water
Total Pressure:
a = 150mm.
b = 318mm.
c = 300mm.
d = 150mm.
OX. No. 5
acetone
c)
formaldehyde
OX. No. 4
d)
acetone
formaldehyde
Product Pressure in R.V. (mm. Hg.)
Time (mins.)

Figure C.25.

FORMALDEHYDE-TIME CURVES : and correlation to other products.

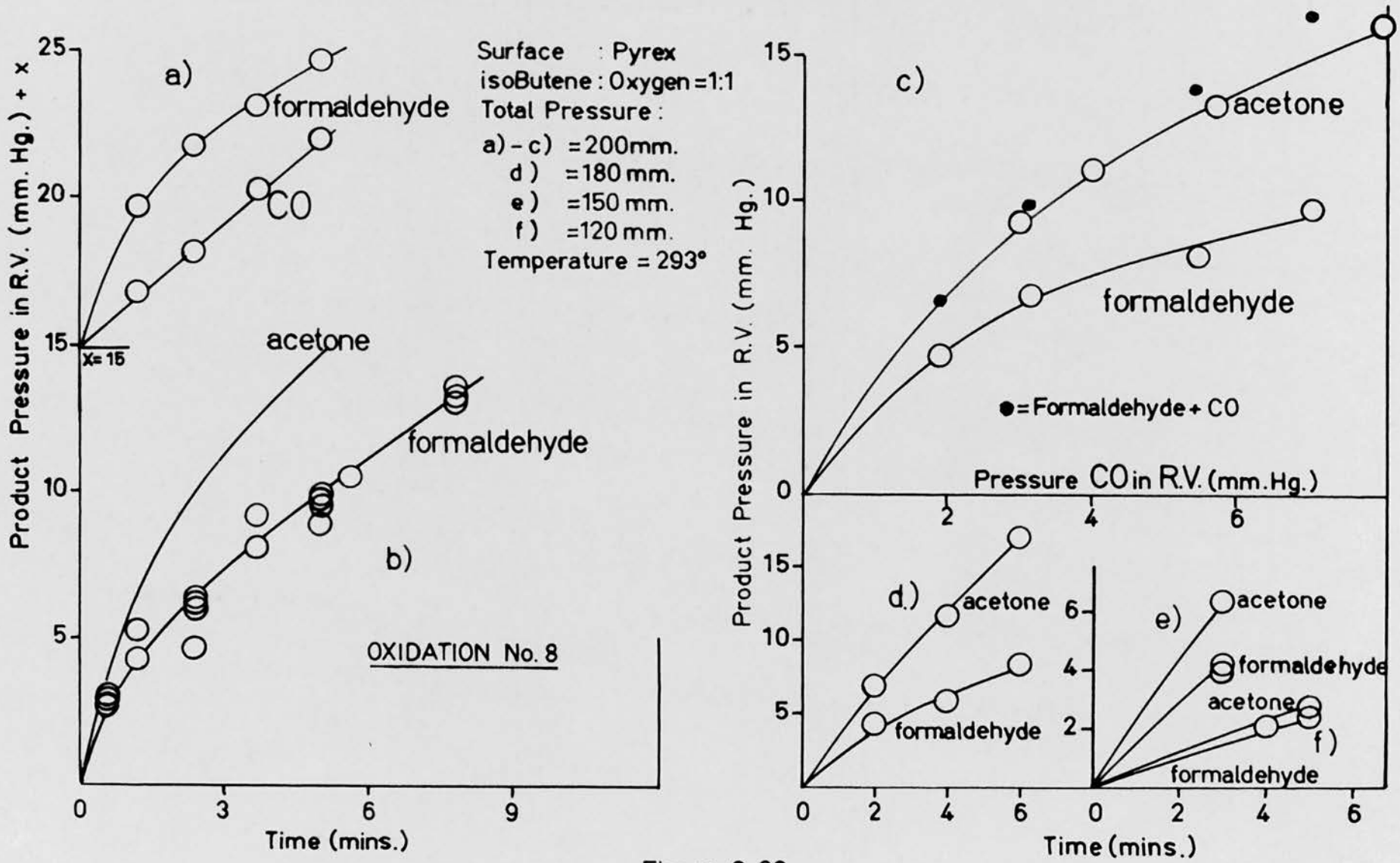


Figure C. 26.

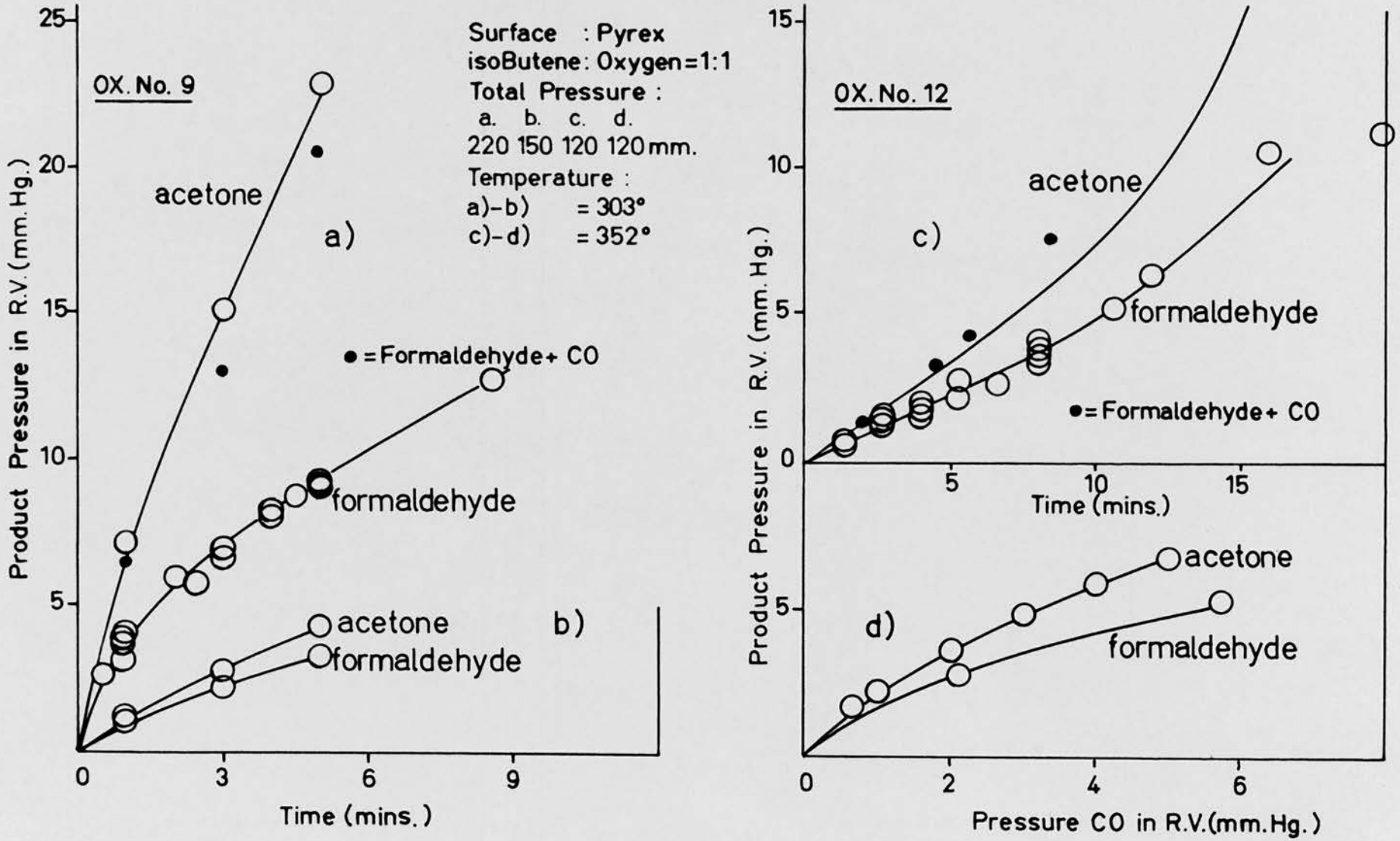
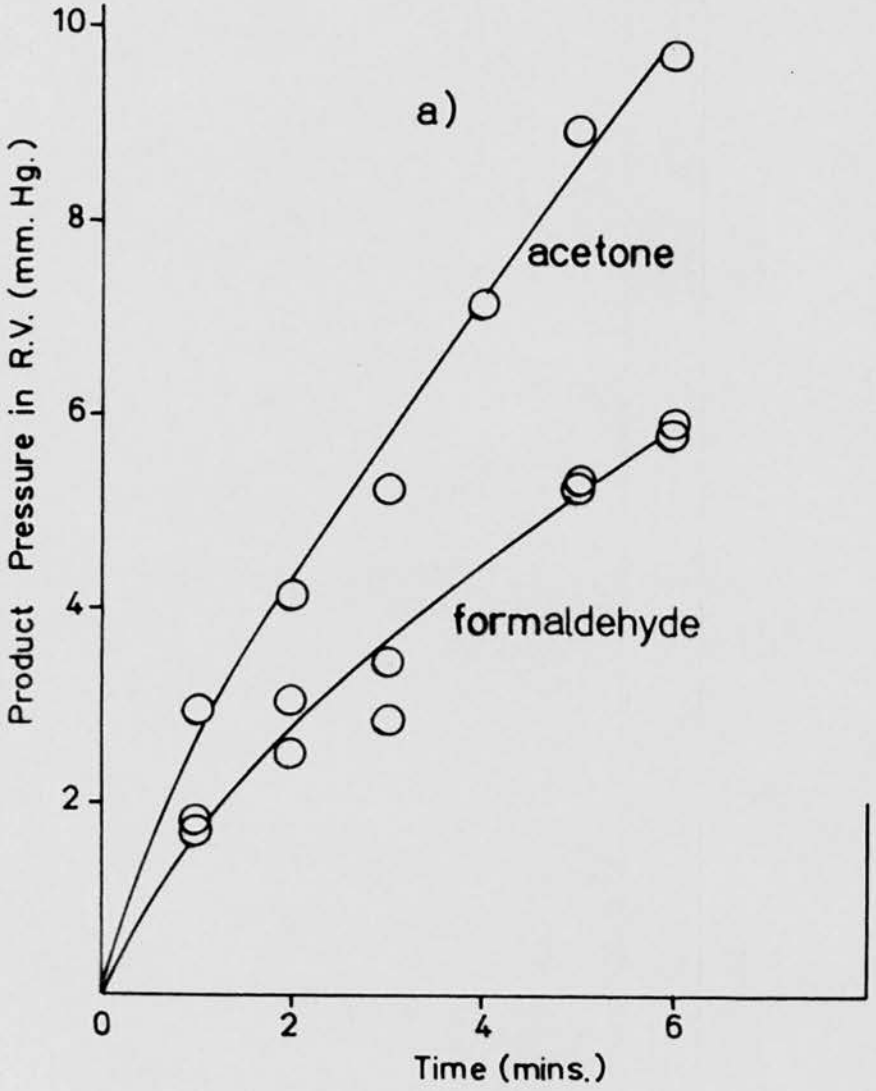

FORMALDEHYDE-TIME CURVES.
OX. No. 9
Surface : Pyrex
isoButene: Oxygen=1:1
Total Pressure :
a. b. c. d.
220 150 120 120 mm.
Temperature :
a)-b) = 303°
c)-d) = 352°
acetone
a)
● = Formaldehyde + CO
formaldehyde
acetone
formaldehyde
b)
Product Pressure in R.V. (mm. Hg.)
Time (mins.)
OX. No. 12
acetone
c)
formaldehyde
● = Formaldehyde + CO
Time (mins.)
acetone
d)
formaldehyde
Product Pressure in R.V. (mm. Hg.)
Pressure CO in R.V. (mm. Hg.)

Figure C.27.

FORMALDEHYDE - TIME CURVES.



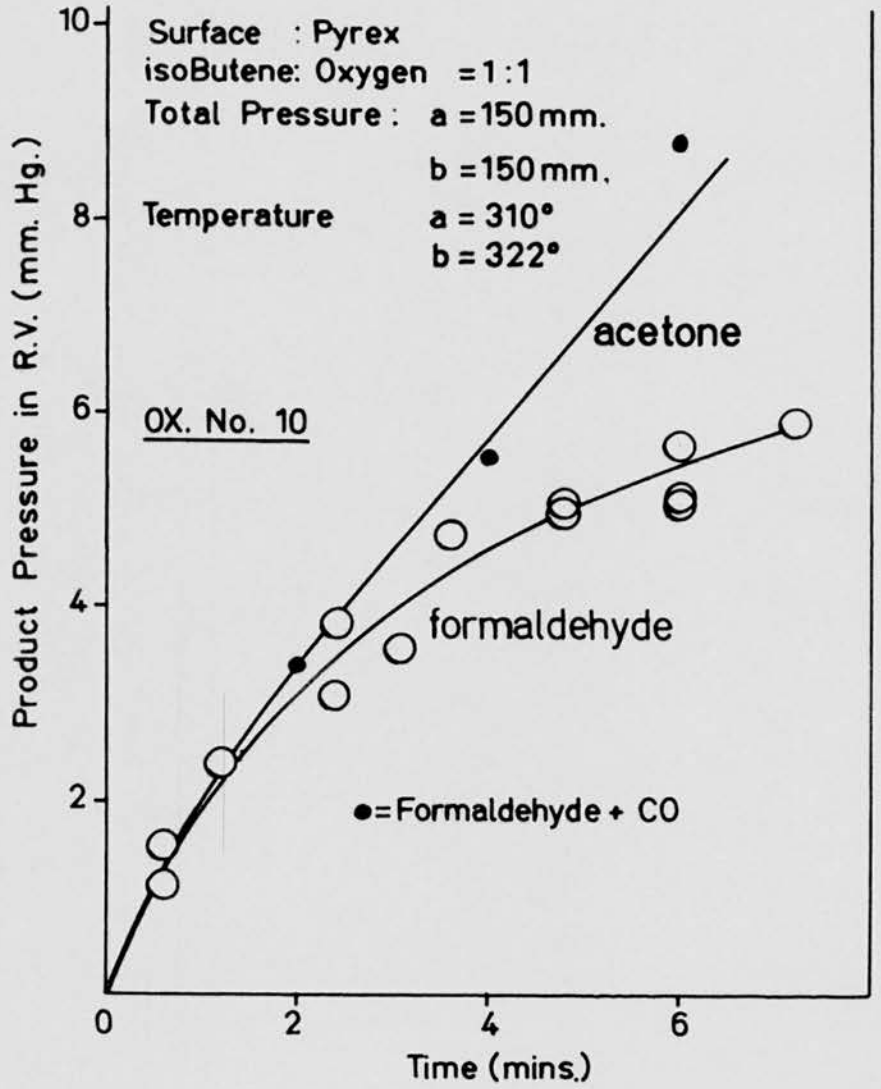


Figure C.28.

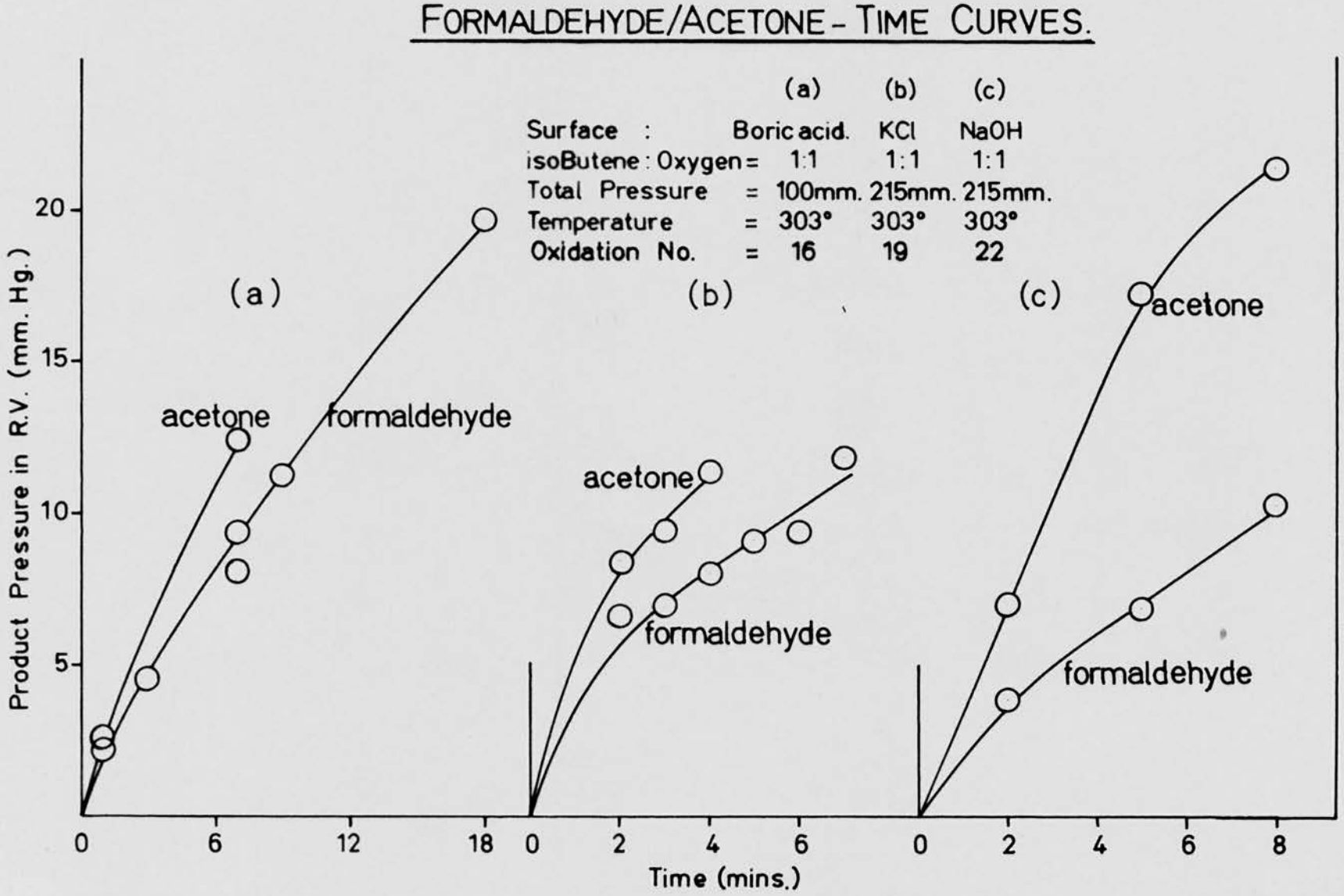

FORMALDEHYDE/ACETONE - TIME CURVES.
(a) (b) (c)
Surface : Boric acid. KCl NaOH
isoButene : Oxygen = 1:1 1:1 1:1
Total Pressure = 100mm. 215mm. 215mm.
Temperature = 303° 303° 303°
Oxidation No. = 16 19 22
(a)
(b)
(c)
acetone
formaldehyde
acetone
formaldehyde
acetone
formaldehyde
Product Pressure in R.V. (mm. Hg.)
20
15
10
5
0
6
12
18
0
2
4
6
0
2
4
6
8
Time (mins.)

Figure C.29.

3. Kinetic Results.

The kinetic results include the effect on the pressure/time curves of :

(a) varying reactant composition, (Figure C. 30),

(b) varying the reaction temperature and total pressure of 1 : 1 mixtures, (Figure C. 31),

(c) varying the nature of the reaction vessel surface (Figure C. 32);

all of which were measured during the course of Oxidation Nos. 1 - 22.

A separate series of kinetic runs, without product analyses, was carried out at 303°. The effect on the following kinetic parameters of varying reactant composition and total pressure of 1 : 1 mixtures was measured :

(a) the overall pressure change, (ΔP_{∞}),

(b) the extent of pressure decrease, (ΔPd),

(c) the maximum rate of pressure increase, (ρmax),

(d) the maximum rate of pressure decrease, (ρd).

The results are given in Table C. 24, and Figures C. 33 - C. 34.

From this data an attempt was made to determine the order of the reaction with respect to the maximum rate of pressure decrease and the maximum rate of pressure increase, (Table C. 25., Figure C. 35).

Figure C.30.

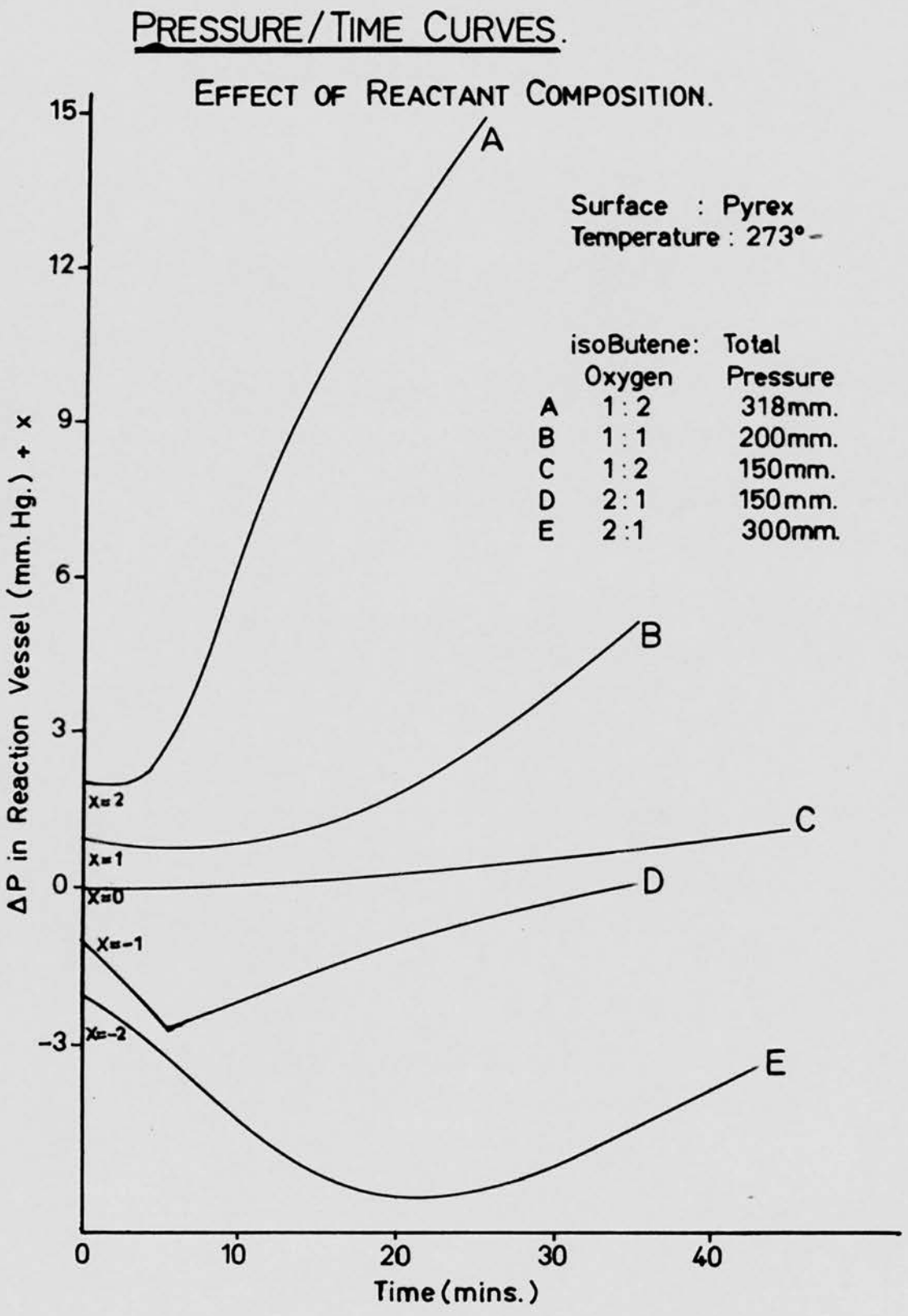

PRESSURE/TIME CURVES.
EFFECT OF REACTANT COMPOSITION.
Surface : Pyrex
Temperature : 273°-
isoButene: Oxygen
Total Pressure
A 1:2 318mm.
B 1:1 200mm.
C 1:2 150mm.
D 2:1 150mm.
E 2:1 300mm.
ΔP in Reaction Vessel (mm.Hg.) + x
Time (mins.)
15
12
9
6
3
0
-3
0
10
20
30
40
X=2
X=1
X=0
X=-1
X=-2
A
B
C
D
E

Figure C.31.

PRESSURE / TIME CURVES.

EFFECT OF TEMPERATURE AND TOTAL PRESSURE.

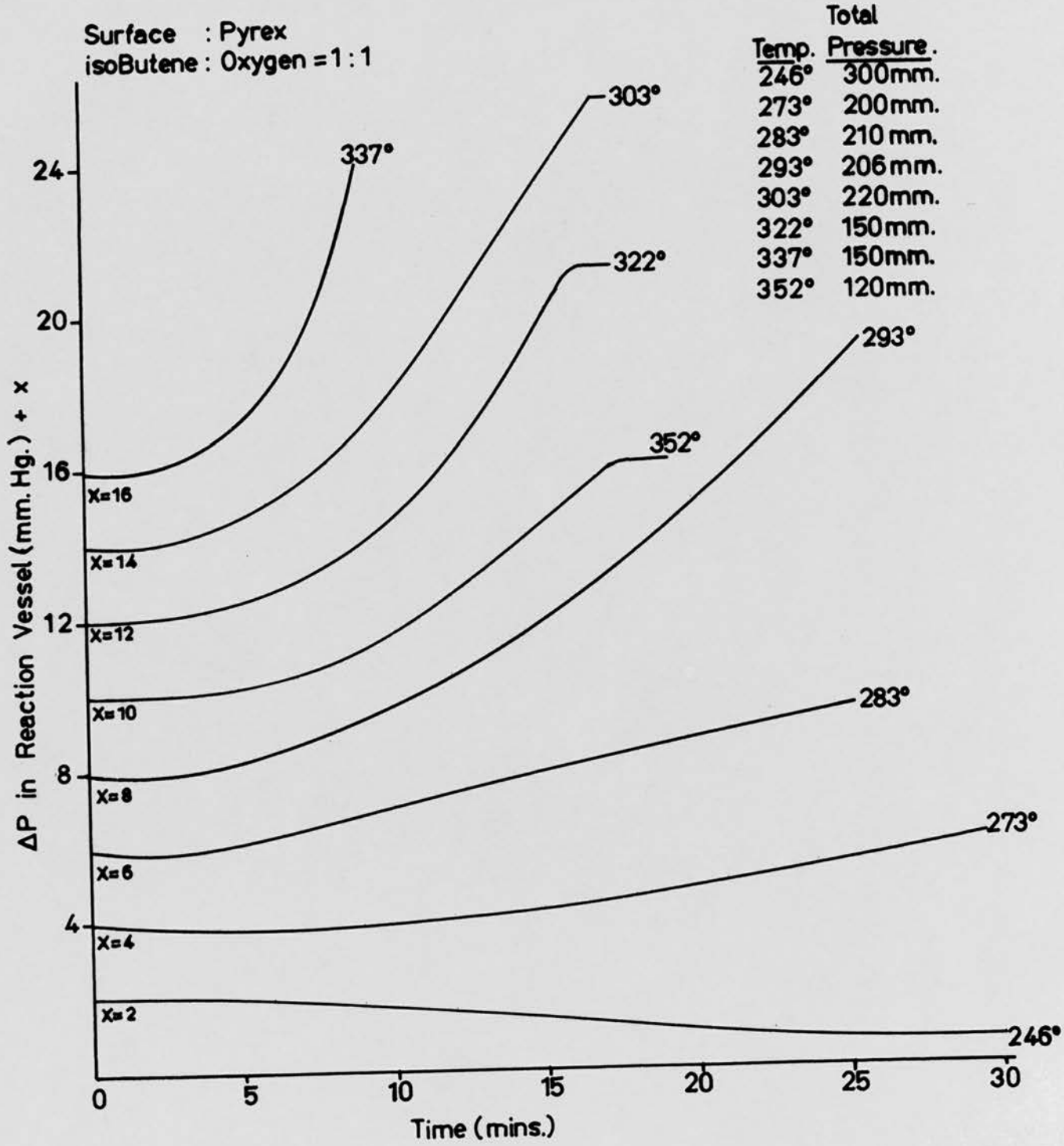


Figure C.32.

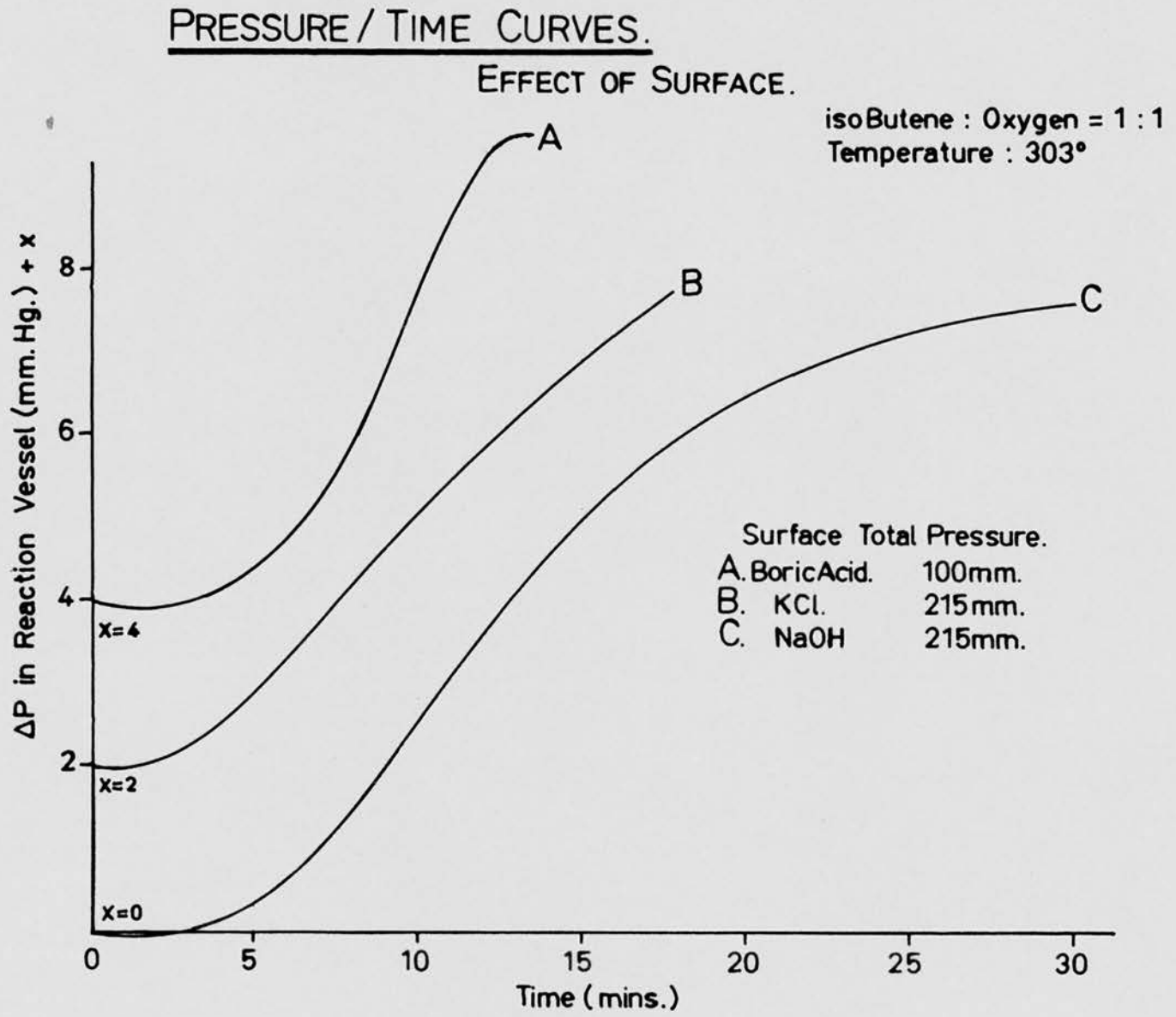

PRESSURE / TIME CURVES.
EFFECT OF SURFACE.
isoButene : Oxygen = 1 : 1
Temperature : 303°
A
B
C
ΔP in Reaction Vessel (mm.Hg.) + x
8
6
4
2
X=4
X=2
X=0
0
5
10
15
20
25
30
Time (mins.)
Surface Total Pressure.
A. BoricAcid. 100mm.
B. KCl. 215mm.
C. NaOH 215mm.

TABLE NO. C. 24 (figures C. 33., C. 34.)

Dependence of kinetic parameters on reactant composition.

Temperature = 303°

Reactant Pressure (mm. Hg.)			ΔP_∞ (mm. Hg.)	ΔP_d (mm. Hg.)	$\rho_{max.}$ (mm/min)	ρ_d. (mm/min)
iC_4H_8	O_2					
100.0	37.5	-	0.71	1.20	0.08	0.17
"	48.5	+	0.57	1.13	0.31	0.26
"	65.9		3.42	1.00	0.86	0.44
"	90.6		9.25	0.60	1.71	0.58
"	132.9		22.5	0.39	3.29	0.59
"	204.0		58.2	0.11	3.67	0.57
24.3	100.0	+	26.4	0.00	0.38	0.00
33.2	"		32.6	0.00	0.48	0.00
41.8	"		32.4	0.00	0.76	0.00
55.6	"		24.2	0.07	1.05	0.12
66.1	"		21.1	0.16	1.38	0.18
101.1	"		11.7	0.48	1.96	0.54
158.8	"		5.20	1.07	1.75	2.42
199.5	"		0.23	2.23	1.74	2.37
49.9	49.9	+	6.19	0.16	0.40	0.06
65.1	65.1		7.87	0.38	0.74	0.18
79.4	79.4		10.0	0.41	1.13	0.31
96.4	96.4		11.8	0.48	1.52	0.50
117.4	117.4		13.6	0.73	2.60	0.92
142.9	142.9		15.5	0.97	3.20	1.77
186.6	186.6		14.9	1.03	2.93	2.44

Figure C. 33.

EFFECT OF REACTANT COMPOSITION ON KINETIC PARAMETERS.

Surface : Pyrex ⊕ Oxygen : 100mm. isoButene : varied.
Temperature : 303° ○ isoButene : 100mm. Oxygen : varied.

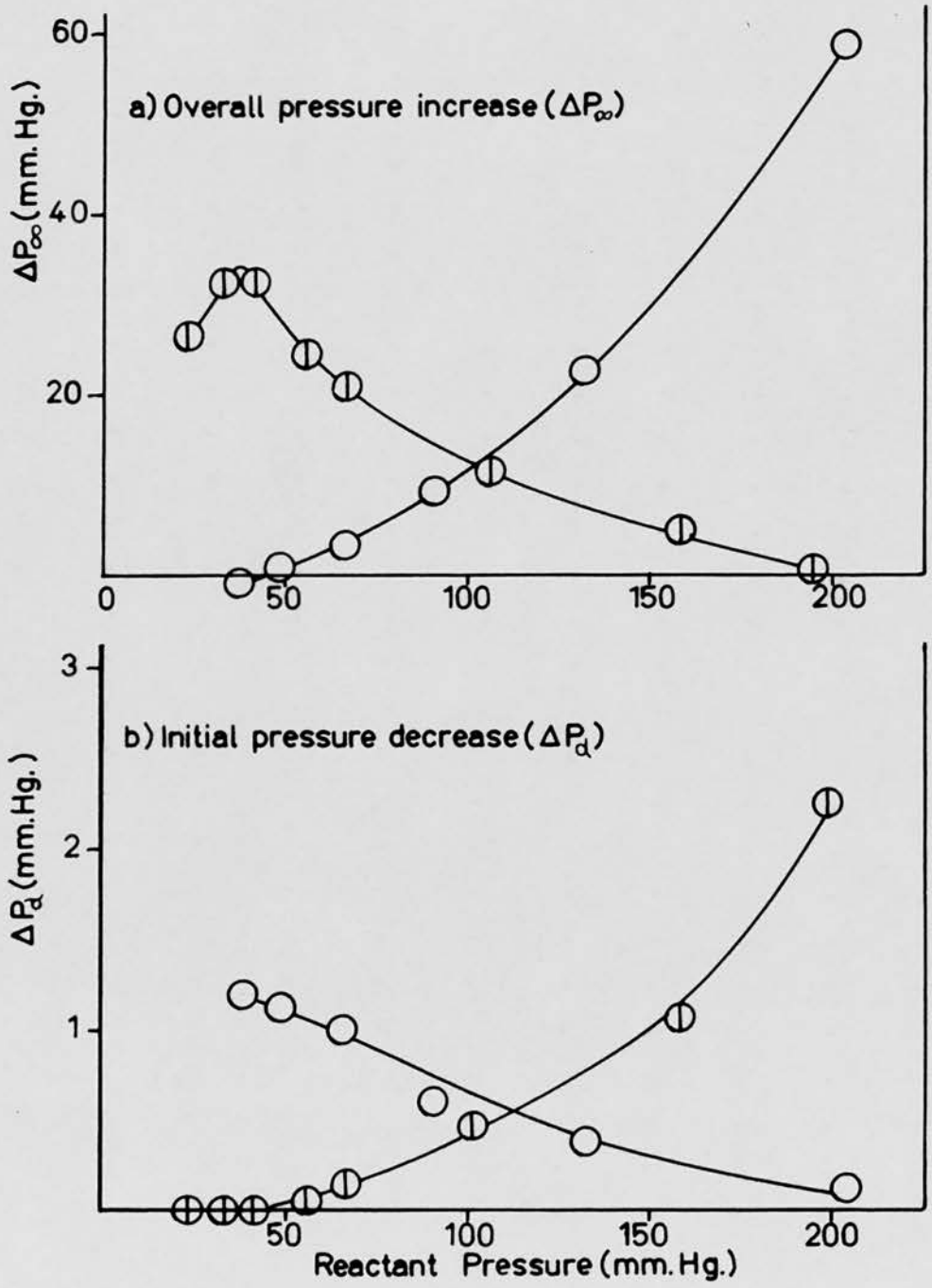


Figure C.34.

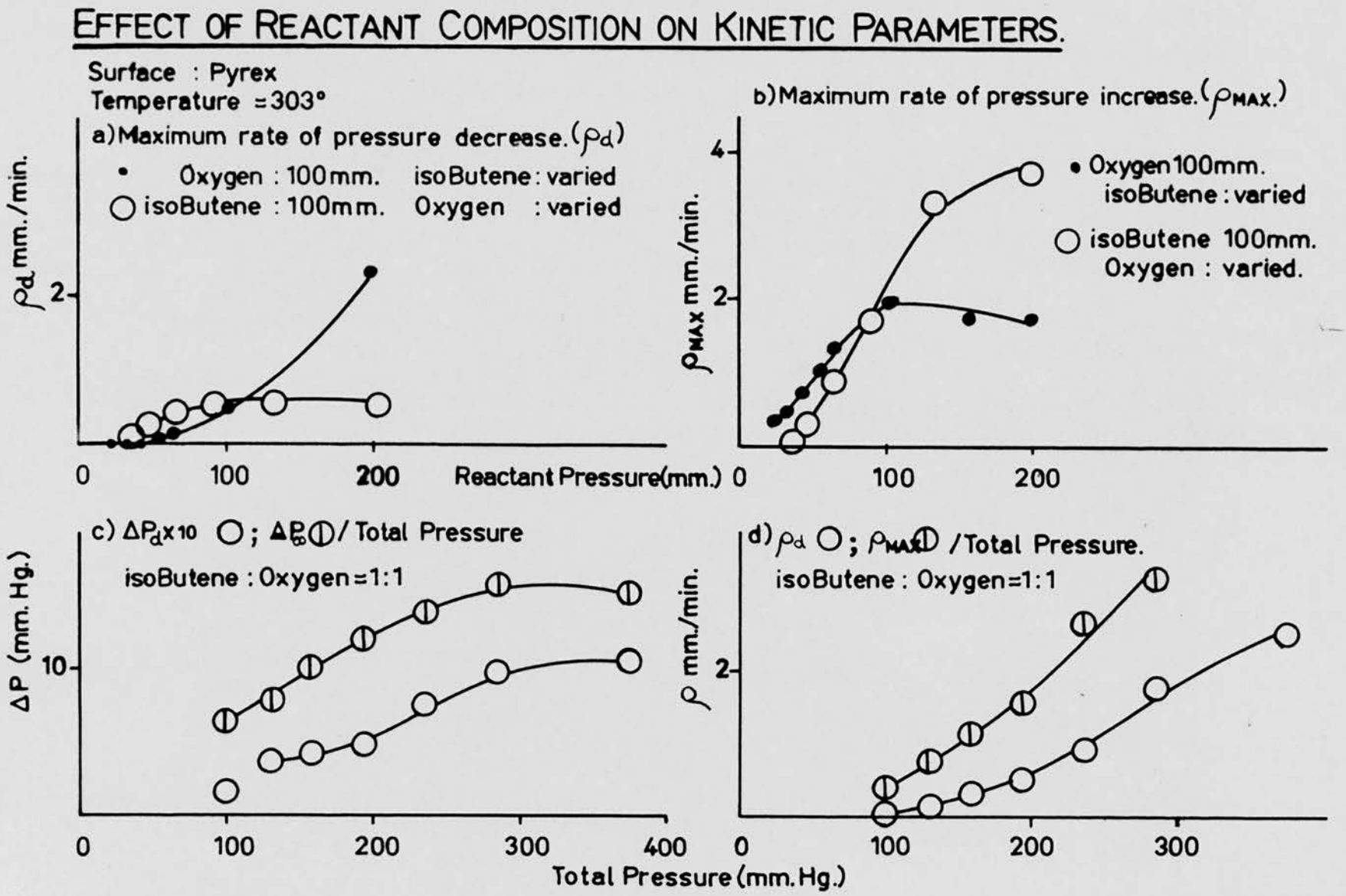

EFFECT OF REACTANT COMPOSITION ON KINETIC PARAMETERS.
Surface : Pyrex
Temperature =303°
a) Maximum rate of pressure decrease. (ρ_d)
• Oxygen : 100mm. isoButene : varied
○ isoButene : 100mm. Oxygen : varied
ρ_d mm./min.
2
0
100
200
Reactant Pressure(mm.)
b) Maximum rate of pressure increase. ($\rho_{MAX.}$)
• Oxygen 100mm. isoButene : varied
○ isoButene 100mm. Oxygen : varied.
ρ_{MAX} mm./min.
4
2
0
100
200
c) $\Delta P_d \times 10$ ○ ; ΔP_∞ ◑ / Total Pressure
isoButene : Oxygen = 1:1
ΔP (mm. Hg.)
10
0
100
200
300
400
Total Pressure (mm. Hg.)
d) ρ_d ○ ; ρ_{MAX} ◑ / Total Pressure.
isoButene : Oxygen = 1:1
ρ mm./min.
2
0
100
200
300

TABLE NO. C. 25 (figure C. 35.)

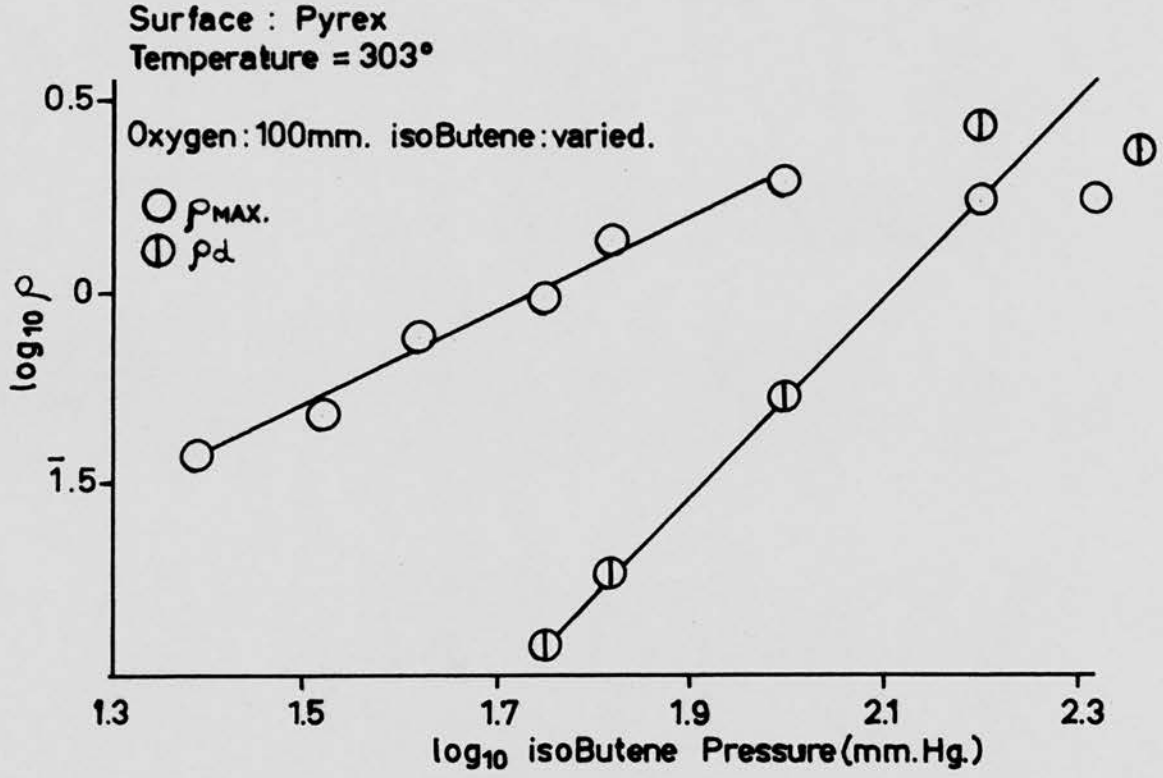
Dependence of kinetic parameters on reactant composition

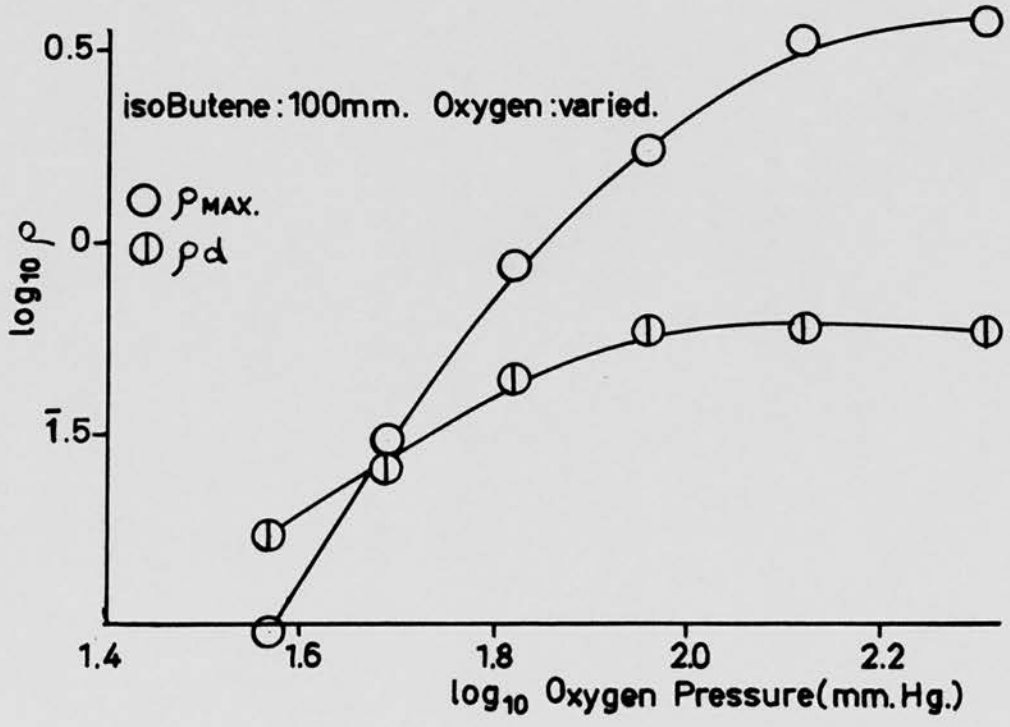
Temperature = 303°

Reactant Pressure (mm. Hg.)		LogiC_4H_8	LogO_2	ρ max. (mm/min)	Log ρ max.	ρd (mm/min)	Log ρ d
iC_4H_8	O_2						
100.0	37.5		1.574	0.08	$\bar{2}$.903	0.17	$\bar{1}$.230
	48.5		1.686	0.31	$\bar{1}$.491	0.26	$\bar{1}$.415
	65.9		1.819	0.86	$\bar{1}$.935	0.44	$\bar{1}$.644
	90.6		1.957	1.71	0.233	0.58	$\bar{1}$.763
	132.9		2.124	3.29	0.517	0.59	$\bar{1}$.771
	204.0		2.310	3.67	0.565	0.57	$\bar{1}$.756
24.3	100.0	1.386		0.38	$\bar{1}$.580	-	-
33.2		1.521		0.48	$\bar{1}$.681	-	-
41.8		1.621		0.76	$\bar{1}$.881	-	-
55.6		1.745		1.05	0.021	0.12	$\bar{1}$.079
66.1		1.820		1.38	0.140	0.18	$\bar{1}$.255
101.1		2.005		1.96	0.292	0.54	$\bar{1}$.732
158.8		2.201		1.75	0.243	2.72	0.435
199.5		2.300		1.74	0.241	2.37	0.375

Figure C. 35.

EFFECT OF REACTANT COMPOSITION ON KINETIC PARAMETERS.





3.1 The order of the reaction

The order of the reaction with respect to oxygen and isobutene pressure was tested for several oxidation runs, the results of which are shown in Figure C.36.

For the five runs at 273° under conditions of varying reactant pressure, (Oxidation Nos. 1-5), log of initial rate, taken as the initial rate of production of acetone in mm. $min.^{-1}$, has been plotted against log X, (Figure C.36a), where X represents the initial pressure of oxygen when that of isobutene is kept constant (Oxidation Nos. 1, 2 and 3), or the initial pressure of isobutene when that of oxygen is kept constant (Oxidation Nos. 1, 4 and 5). A common line satisfies the two sets of points giving the initial reaction rate an oxygen and isobutene dependence of about 1.5 on each reactant.

For oxidation No. 7, a plot of rate of formation of acetone at different stages in the run against the product of oxygen and isobutene pressures at the same stages in the run (Figure C.36b), shows that the ratio of rate of production of acetone/the product of oxygen and isobutene pressures is constant until a relatively late stage in the oxidation and Figure C.36c shows a test for second order kinetics on the same run. In this plot a = average component starting pressure $(P_{O_2} + P_{C_4})/2$ and x = $(P_{O_2} + P_{C_4})/2$ at any time 't' during the run.

Figures C.36a and C.36b exemplify the different type of reaction

occurring above and below 300° the significance of which will be discussed later.

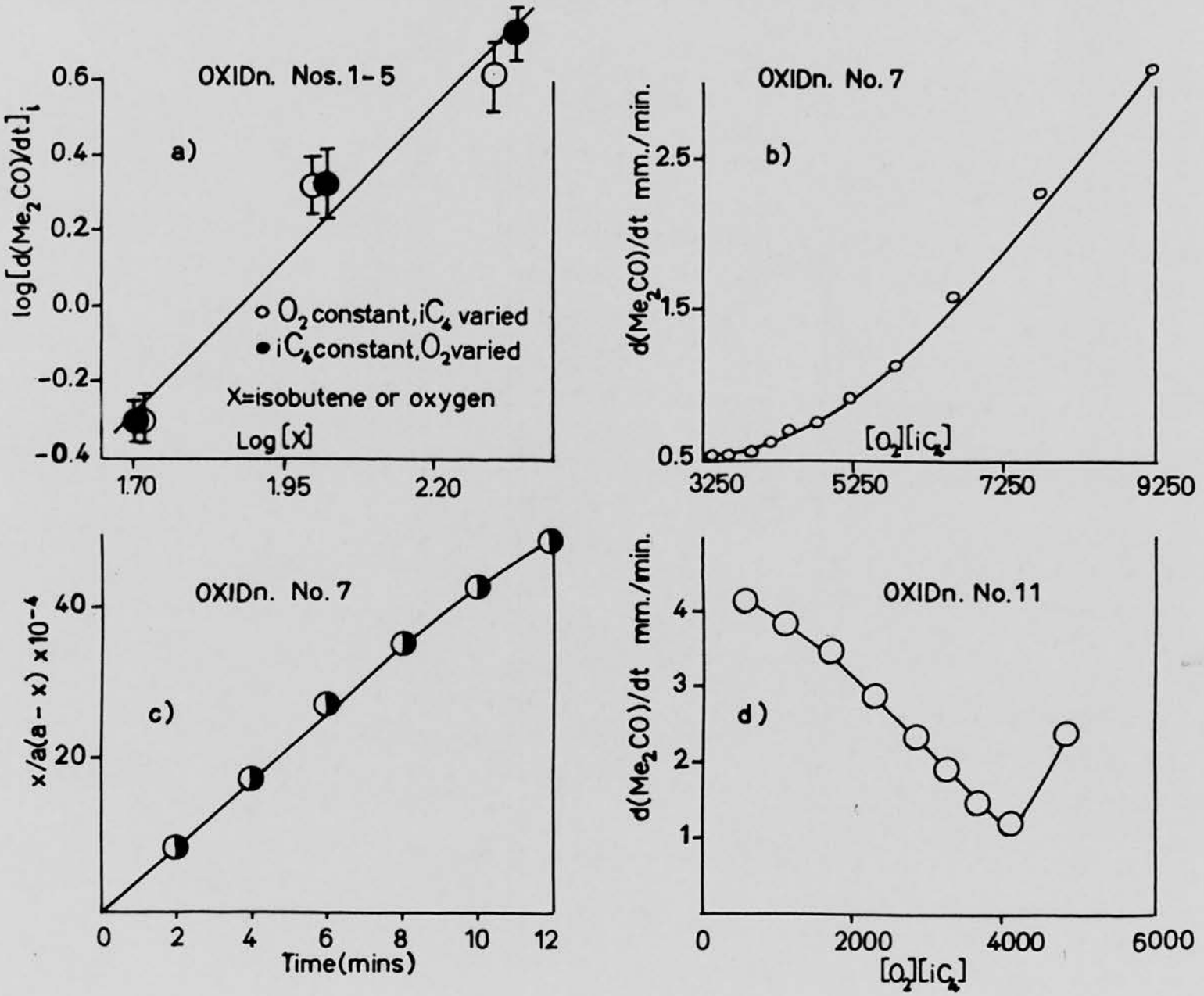

OXIDn. Nos. 1-5
a)
log[d(Me2CO)/dt]i
0.6
0.4
0.2
0.0
-0.2
-0.4
1.70
1.95
2.20
o O2 constant, iC4 varied
• iC4 constant, O2 varied
X=isobutene or oxygen
Log [X]
OXIDn. No. 7
b)
d(Me2CO)/dt mm./min.
2.5
1.5
0.5
3250
5250
7250
9250
[O2][iC4]
OXIDn. No. 7
c)
x/a(a-x) x10-4
40
20
0
2
4
6
8
10
12
Time(mins)
OXIDn. No. 11
d)
d(Me2CO)/dt mm./min.
4
3
2
1
0
2000
4000
6000
[O2][iC4]

Figure C. 36.

4. Isomerisation of isobutene oxide

The apparent replacement of isobutene oxide by isobutyraldehyde in the products from Oxidations 14 - 16 in a boric acid coated vessel, made necessary a study of the rate of isomerisation of isobutene oxide in coated vessels to establish whether or not the changes were due to a change in mechanism or to surface isomerisation.

Isomerisation of the oxide was carried out in the sodium hydroxide coated vessel at 309°, 325° and 356°, and tested for first order kinetics, (Table No. C.26., Figure C.36). A rough measure of the activation energy of the isomerisation was obtained from the Arrhenius plot of log rate constant against reciprocal of absolute temperature. (Figure C.36 inset.)

At 309° and 359° oxidations were carried out on isobutene/oxygen mixtures containing some isobutene oxide, (Table C.27), from which the origin of the isobutyraldehyde was established.

The isomerisation rate in a boric acid coated vessel was extremely fast, about 90% of the isobutene oxide up to pressures of 90 mm.Hg. being converted to isobutyraldehyde inside one minute. Similarly in oxidation runs of isobutene/oxygen mixtures containing isobutene oxide, almost all of the oxide was converted to isobutyraldehyde inside one minute of reaction.

TABLE NO. C. 26. (figure C. 36.)

Isomerisation of isoButene Oxide.

Temp °C	Time from start sec. x10^{-3}	a (mm. Hg.)	x (mm. Hg.)	100x Ln. a/(a-x)
309°	0.00	91.20	0.00	0.00
	4.50		0.86	0.97
	8.28		1.44	1.61
	11.28		1.74	1.96
	15.00		2.38	2.67
	18.00		2.95	3.29
	21.00		3.16	3.55
	25.20		3.81	4.28
	28.20		4.39	4.96
	33.42		5.39	6.12
325°	0.00	90.00	0.00	0.00
	1.86		1.23	1.38
	3.60		2.20	2.47
	5.40		3.20	3.62
	7.56		4.40	4.77
	9.42		5.36	6.14
	11.28		6.30	7.26
	13.68		7.60	8.85
	15.48		8.71	10.20
356°	0.00	90.20	0.00	0.00
	1.92		4.81	5.49
	3.60		7.99	9.26
	7.50		15.7	19.20
	9.30		19.9	25.00
	11.10		23.5	30.30
	13.20		27.2	35.90
	15.60		32.3	44.45
	18.72		39.2	57.00

Figure C.37.

ISOMERISATION OF isoBUTENE OXIDE.

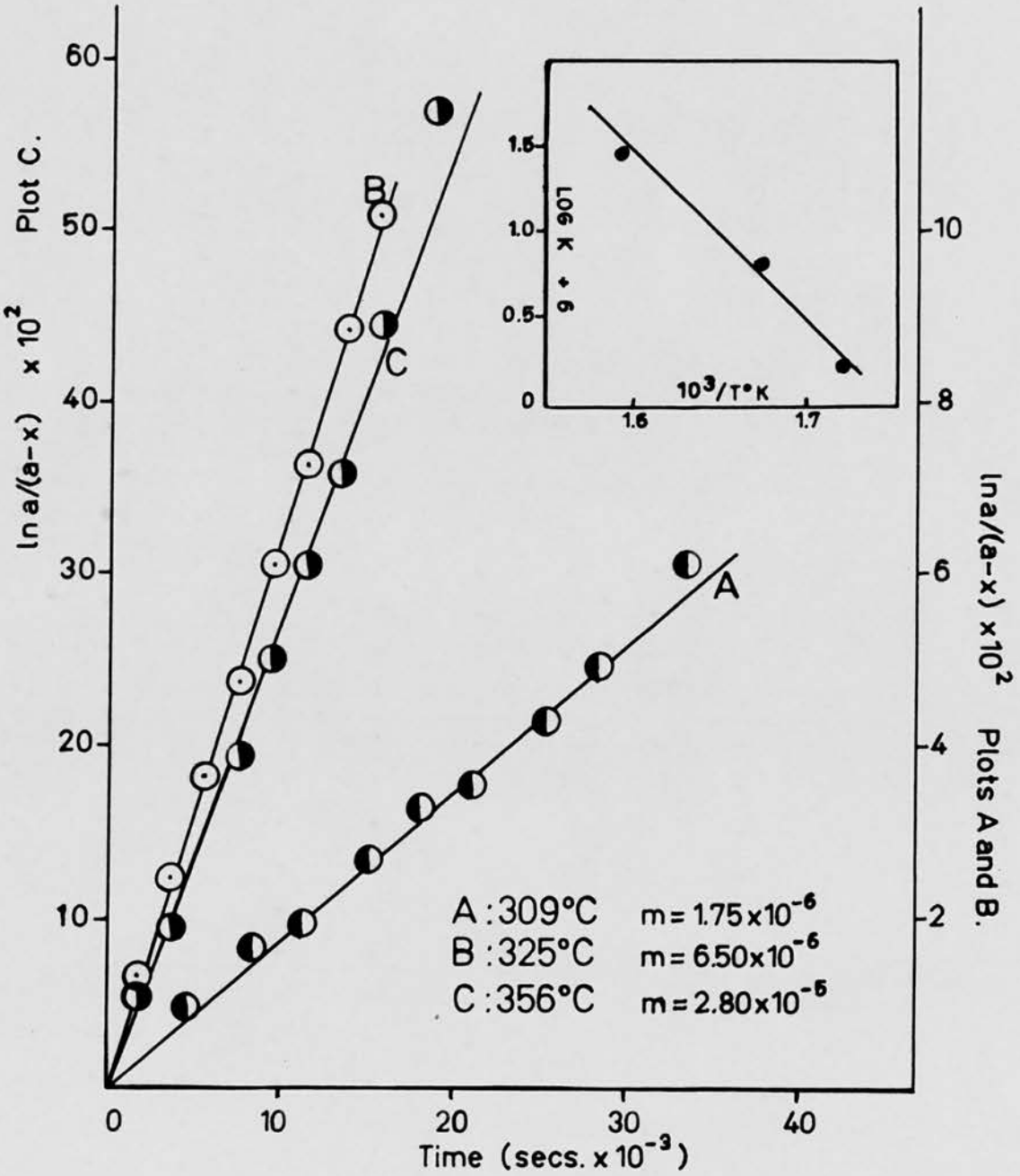


TABLE NO. C.27

Oxidation of mixtures containing isoButene Oxide

Reaction mixture: iC_4H_8 = 183.8mm. O_2 = 202.6mm. iC_4H_8) = 18.3 mm.

Pressure (mm. Hg.)	Temp. °C	Time (mins.)	iC_3H_7CHO (mm. Hg.)	Me_2CO (mm. Hg.)
197.2	309°	0	0.00	0.00
		5	0.43	16.6
		10	0.54	25.6
		15	0.63	34.4
		20	0.74	41.0
		25	0.85	46.5
		30	0.92	46.5
		35	-	48.1
		40	1.08	48.5
166.7	359°	o	0.00	0.00
		5	0.45	7.95
		10	0.67	14.9
		15	0.80	22.0
		20	0.74	24.9

SECTION D

CO-ORDINATION OF RESULTS

1. Co-ordination of Results.

In olefin oxidations it is particularly difficult to obtain a good parameter for following the course of the reaction. Pressure/time curves exhibit an initial pressure decrease and at first sight it would appear that dp/dt bears little relationship to d(reactant)/dt, or d(product)/dt. An examination of the relationship, however, in Oxidation Nos. 10, 11 Figure D.O. shows that there exists some relationship between the parameters, e.g. (dp/dt)max occurs at approximately the same time as $(d0_2/dt)$max and (dMe_2C0/dt)max. A further test of the results of Oxidations 1 - 5, (Figure D.O.c), however, showed that the proportionality factor between $(d0_2/dt)/(dp/dt)$ was not constant enough to justify the use of rate of pressure change as a measure of the reaction rate.

Co-ordination between separate oxidations has been made by the method of 'Initial Product Analysis', (see section A.1.12.).

The carbon content of each product at any time during a run is plotted against the total carbon in the products at the same time in the run. The carbon content expressed as mm.-atom of carbon is obtained by multiplying the pressure of the product, (mm.Hg.), by the number of carbon atoms in the product molecule.

In the present case where all the products except formaldehyde were analysed by gas chromatography and since formaldehyde was not analysed in every oxidation, total carbon in Figures D.1.-D.33. refers to total carbon in the products minus formaldehyde, except Figures D.2. and D.8. which

dP/dt as a measure of reaction rate.

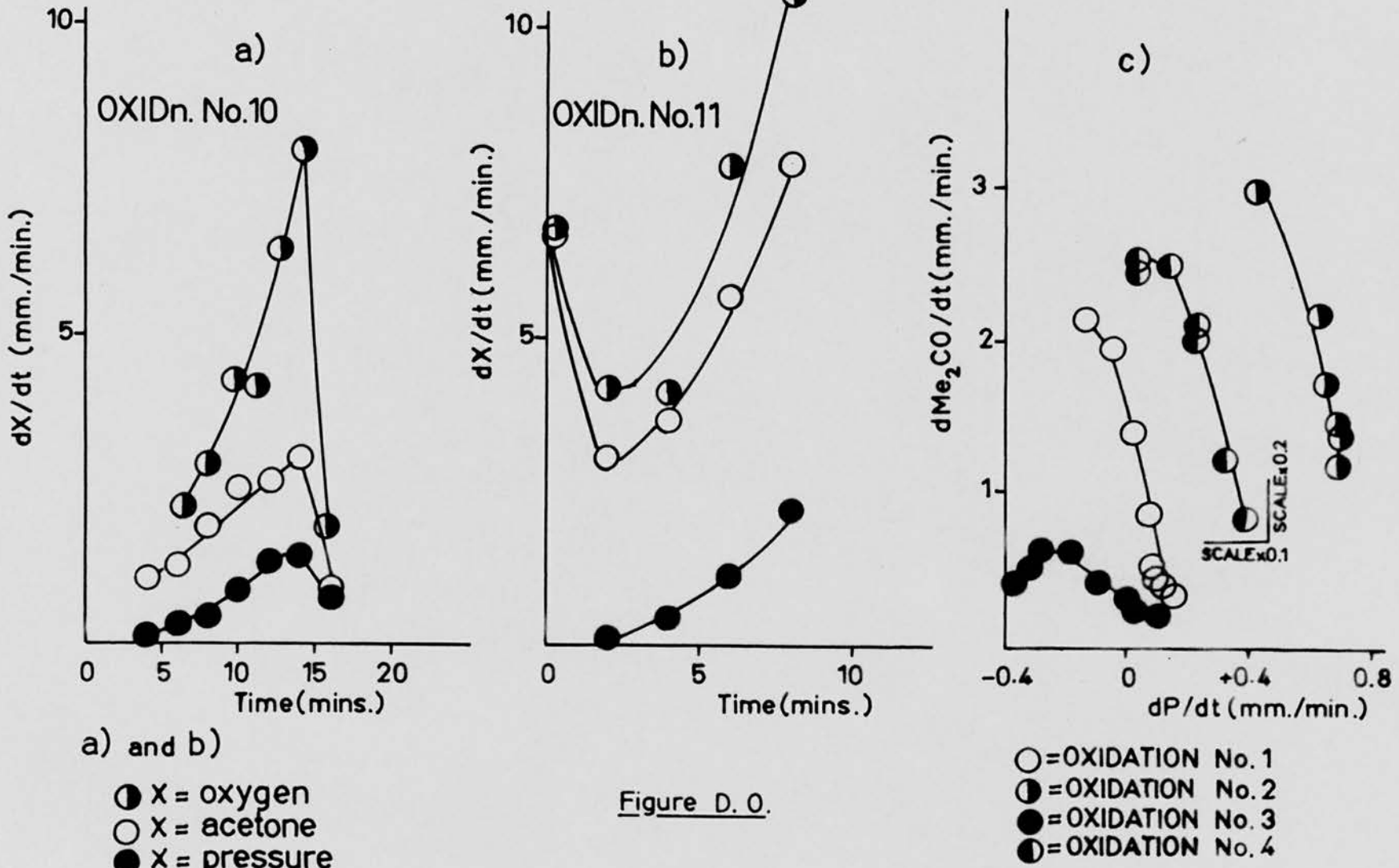


Figure D. 0.

represent carbon content of formaldehyde/total carbon in the products which must then include formaldehyde.

The initial gradients from such curves then gives the relative initial rates of production of each product in terms of the carbon content of all the products.

1.1 The effect of varying reactant composition

Figures D.1. - D.6. represent the effect on the initial yields of products of varying reactant composition, corresponding to Oxidations Nos. 1 - 5.

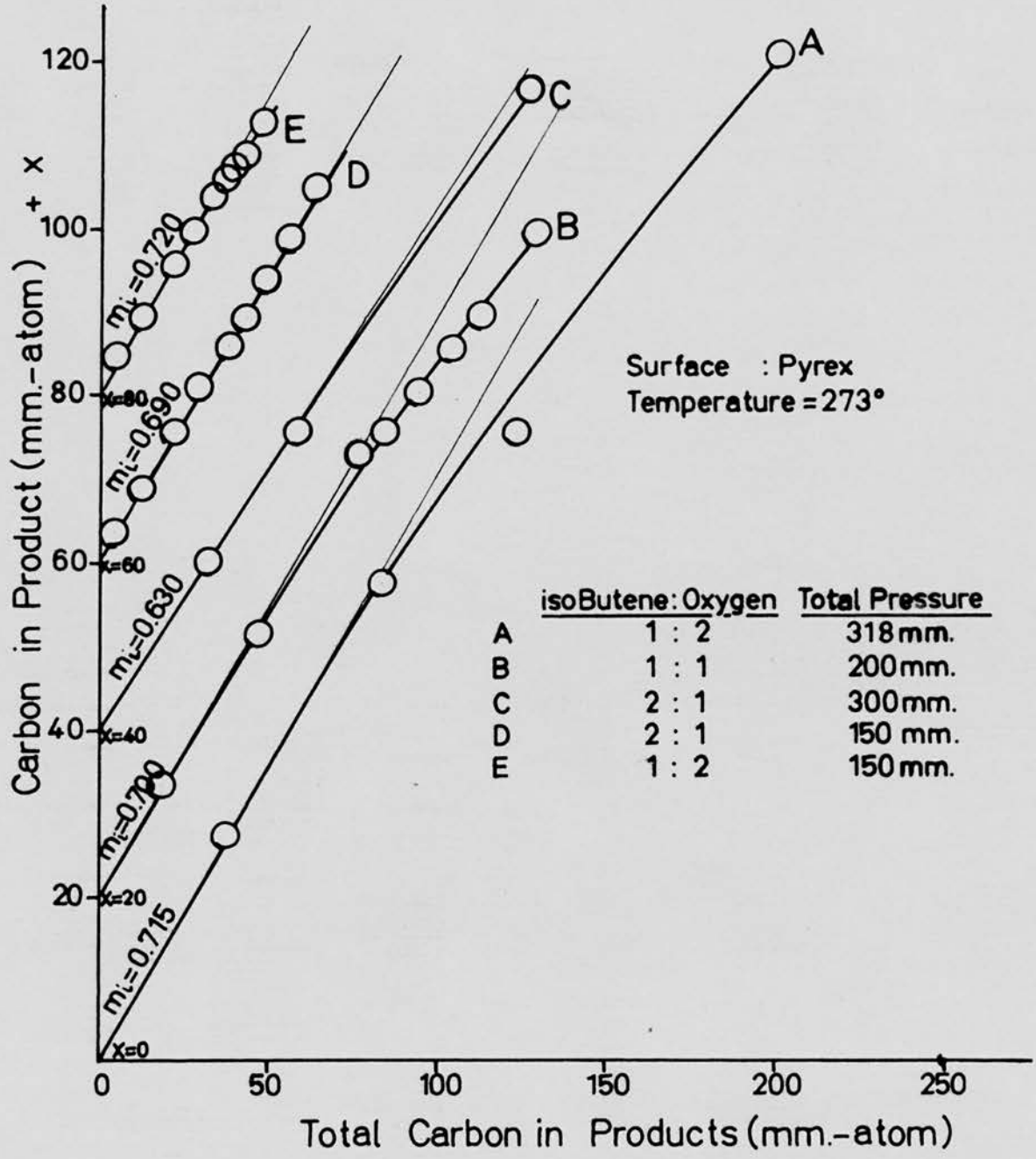
The values on the curves marked A - E were obtained from the following oxidations:

Oxidation	No. 1	=	Curve B
"	No. 2	=	" A
"	No. 3	=	" D
"	No. 4	=	" E
"	No. 5	=	" C

Figure D.1.

EFFECT OF REACTANT PRESSURE ON OXIDATION PRODUCTS.

Product: ACETONE.



	isoButene : Oxygen	Total Pressure
A	1 : 2	318 mm.
B	1 : 1	200 mm.
C	2 : 1	300 mm.
D	2 : 1	150 mm.
E	1 : 2	150 mm.

Figure D.2.

EFFECT OF REACTANT PRESSURE ON OXIDATION PRODUCTS.

Product :
FORMALDEHYDE.

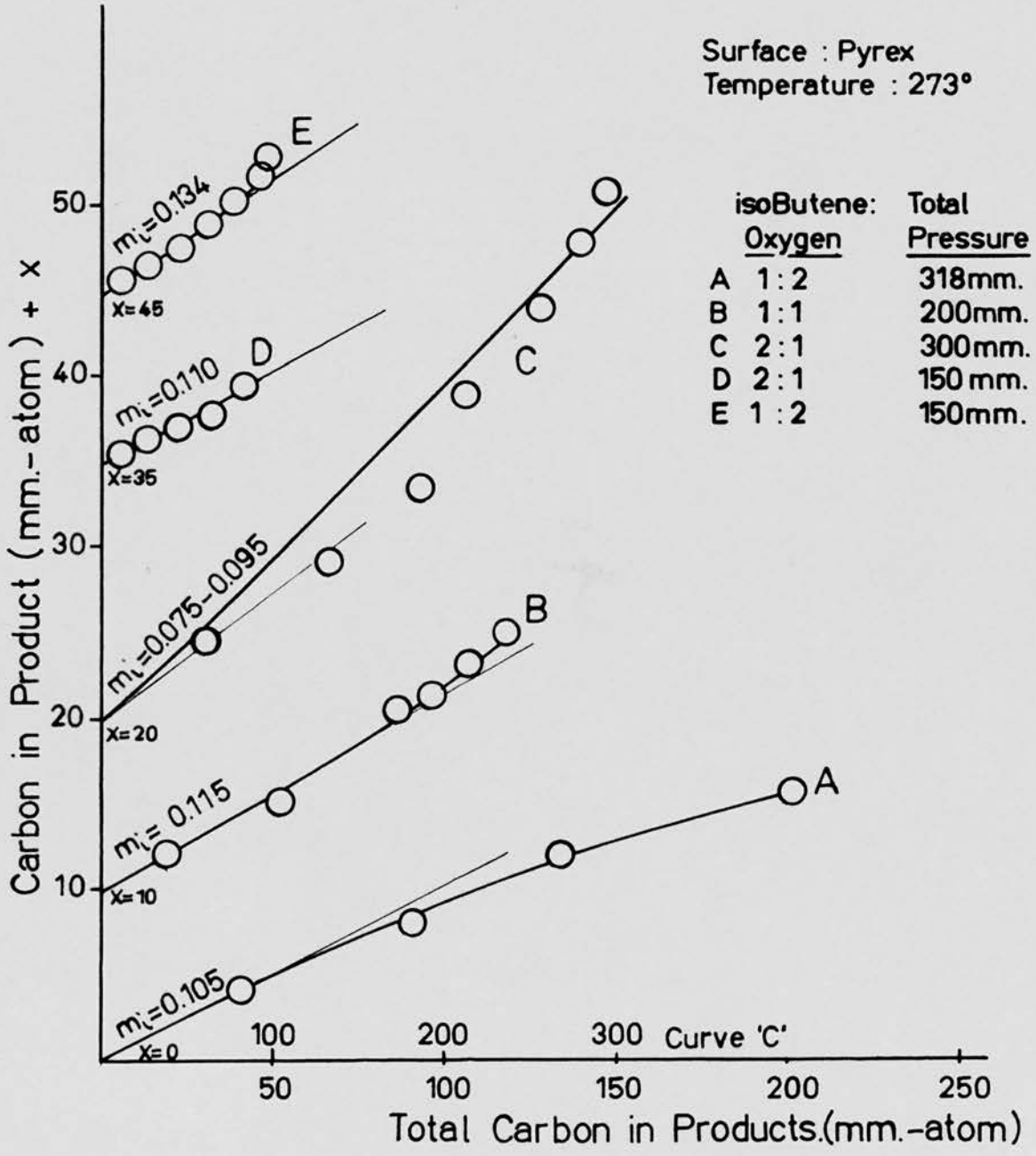


Figure D.3.

EFFECT OF REACTANT PRESSURE ON OXIDATION PRODUCTS.

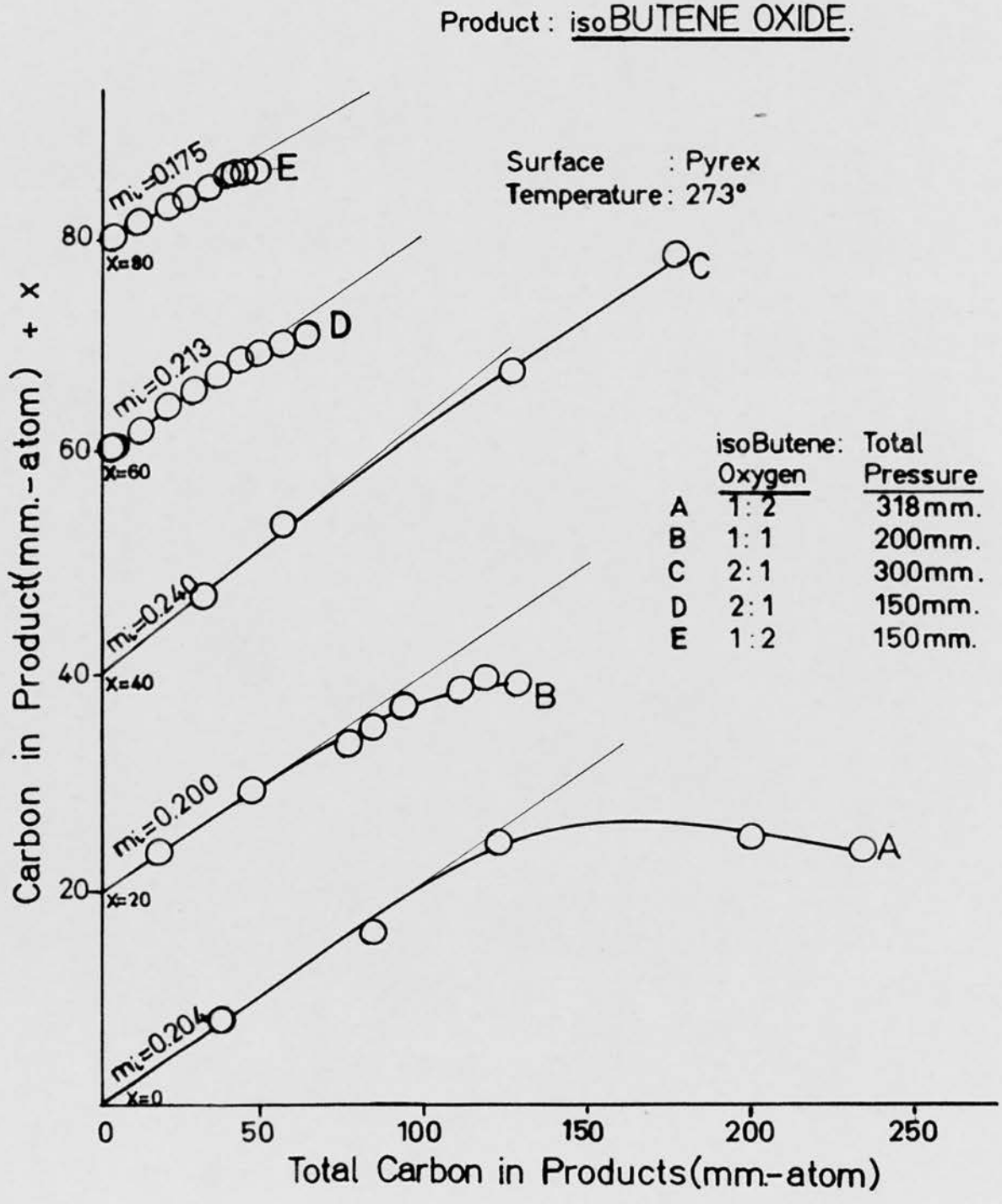


Figure D.4.

EFFECT OF REACTANT PRESSURE ON OXIDATION PRODUCTS.

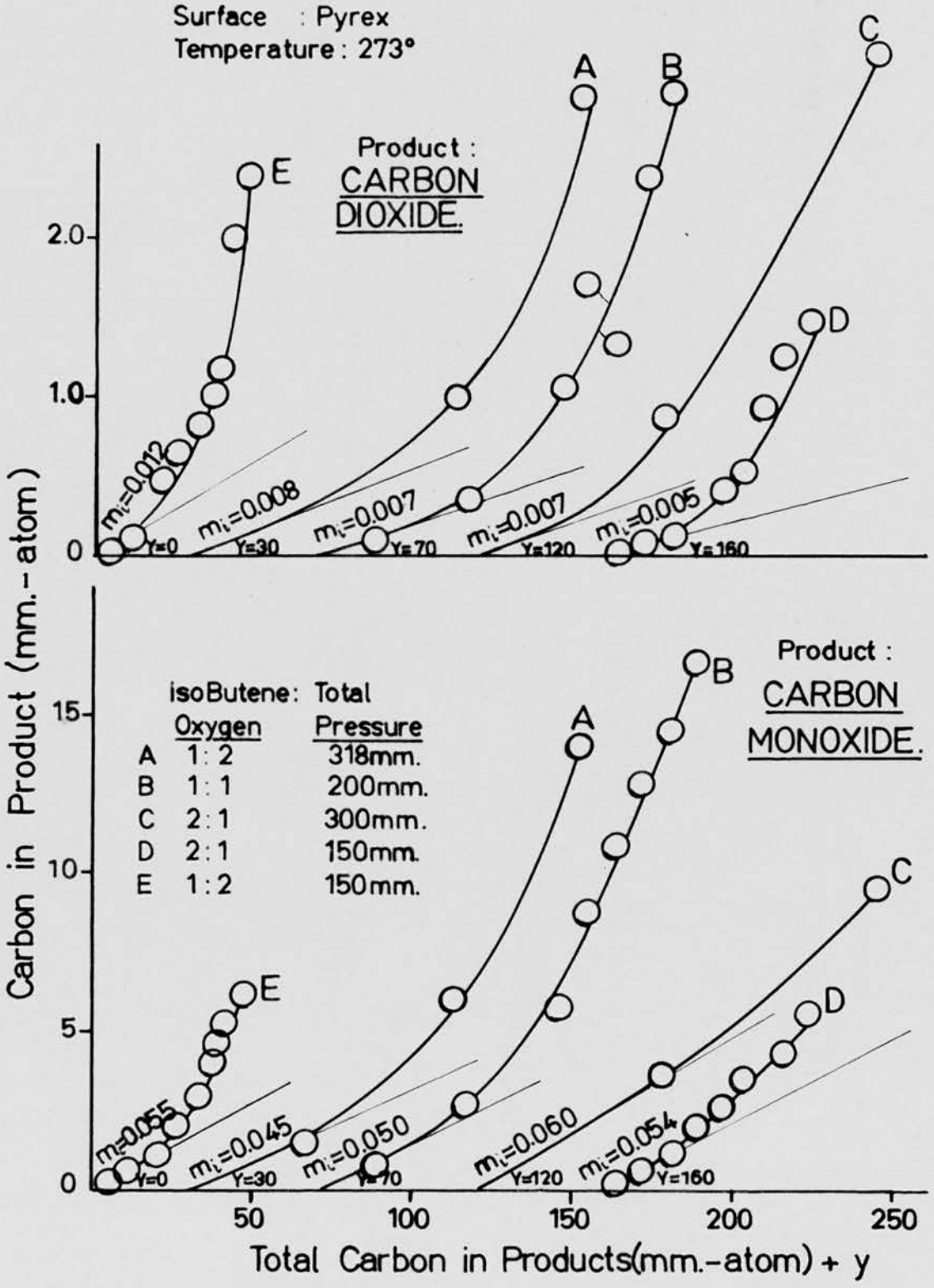


Figure D.5.

EFFECT OF REACTANT PRESSURE ON OXIDATION PRODUCTS.

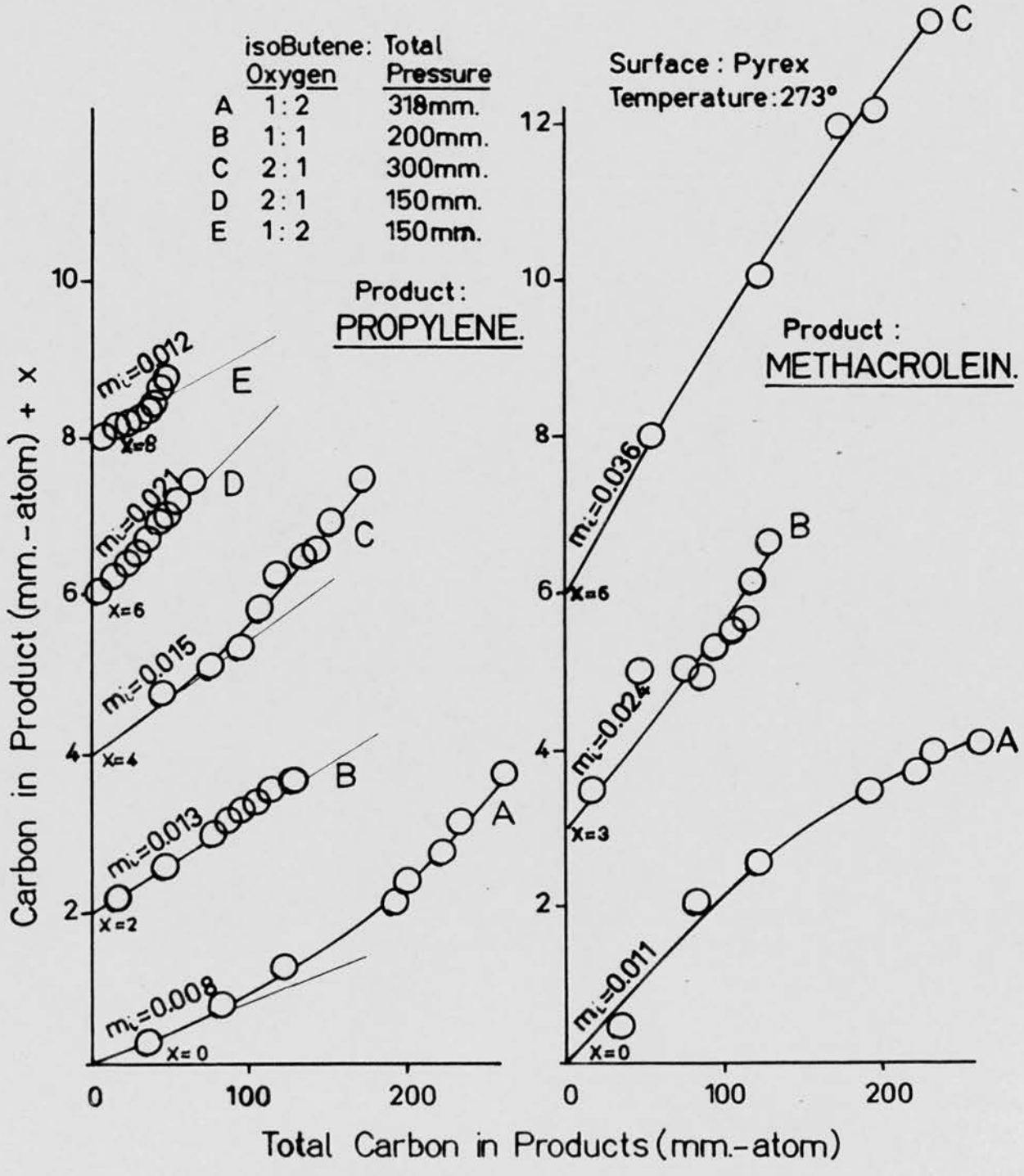
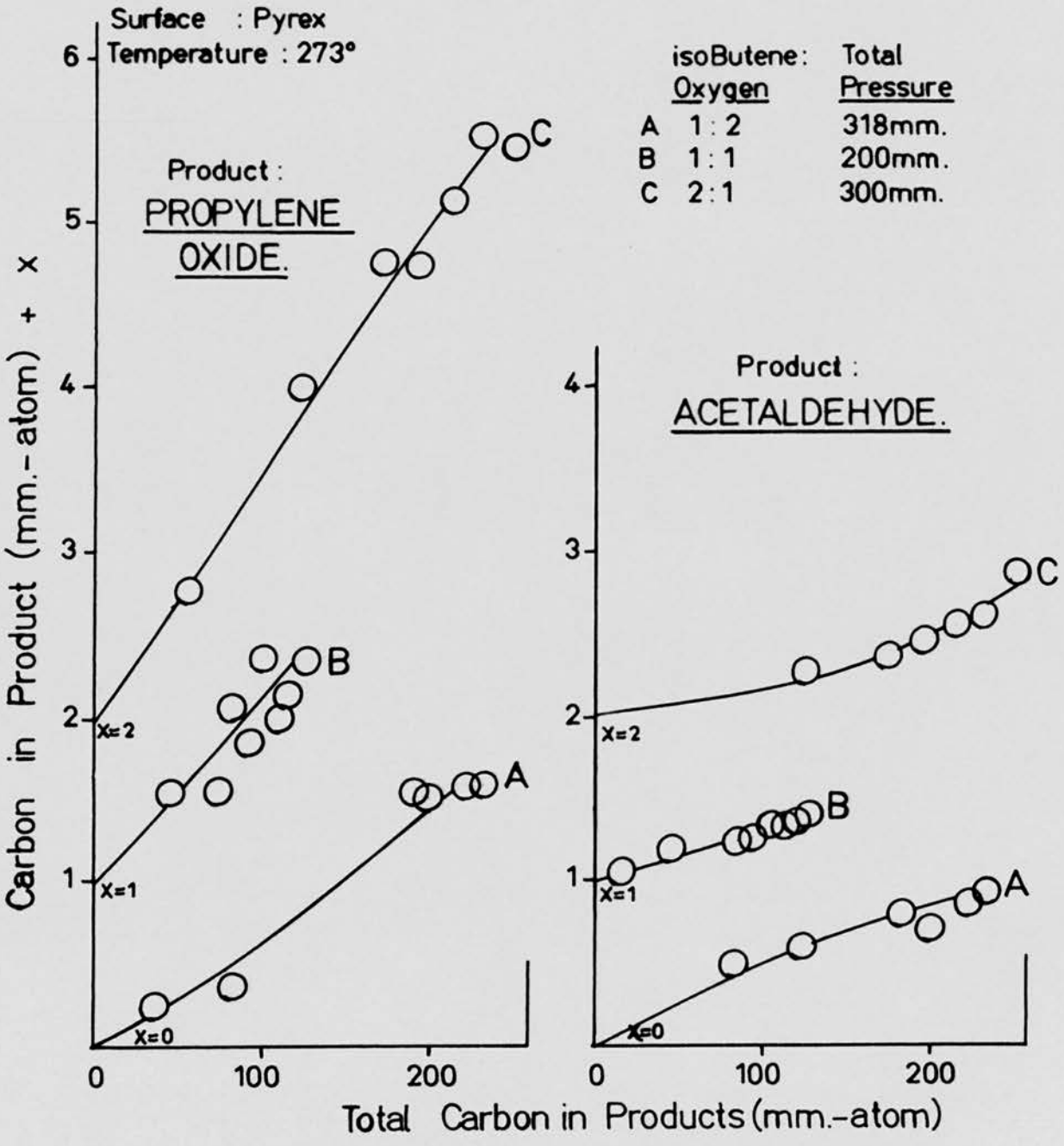


Figure D.6.


EFFECT OF REACTANT PRESSURE ON OXIDATION PRODUCTS.
Surface : Pyrex
Temperature : 273°
isoButene: Oxygen
Total Pressure
A 1:2 318mm.
B 1:1 200mm.
C 2:1 300mm.
Product : PROPYLENE OXIDE.
Product : ACETALDEHYDE.
Carbon in Product (mm.-atom) + x
Total Carbon in Products (mm.-atom)
X=0
X=1
X=2
0
100
200
1
2
3
4
5
6
A
B
C

1.2 The effect of temperature

Figures D.7. - D.14. represent the effect on the initial yields of products of varying the reaction temperature.

The experimental values on the curves marked A - H were obtained from the following oxidations:

Oxidation	No. 1	=	Curve B
"	No. 7	=	" C
"	No. 8	=	" D
"	No. 9	=	" E
"	No. 10	=	" F
"	No. 11	=	" G
"	No. 12	=	" H
"	No. 13	=	" A

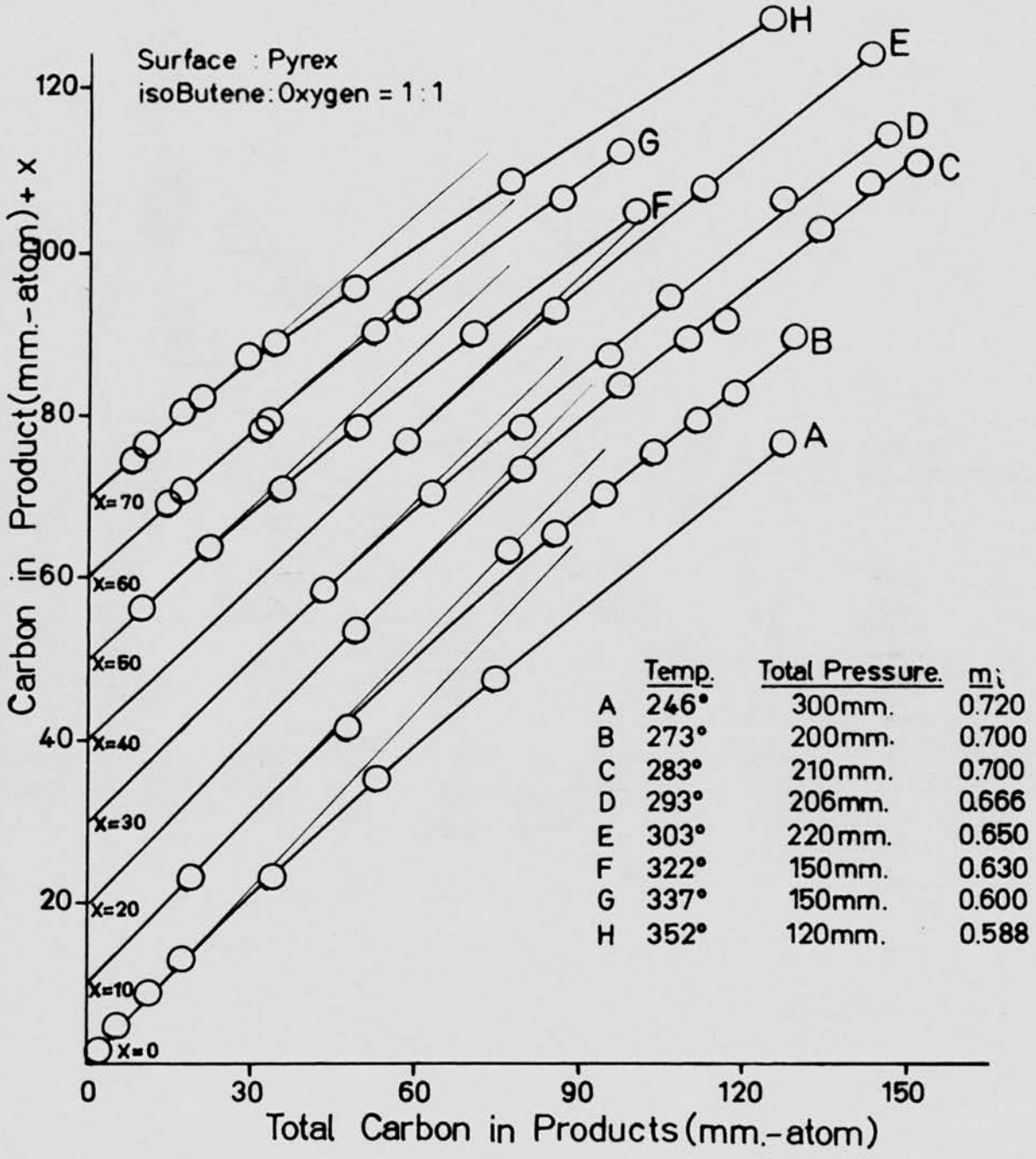
For Figure D.8. the curve markings are as follows:

Oxidation	No. 1	=	Curve B
"	No. 8	=	" C
"	No. 9	=	" D
"	No. 10	=	" E
"	No. 12	=	" F
"	No. 13	=	" A

Figure D.7.

EFFECT OF TEMPERATURE ON OXIDATION PRODUCTS.

Product : ACETONE.



	Temp.	Total Pressure.	m_i
A	246°	300mm.	0.720
B	273°	200mm.	0.700
C	283°	210mm.	0.700
D	293°	206mm.	0.666
E	303°	220mm.	0.650
F	322°	150mm.	0.630
G	337°	150mm.	0.600
H	352°	120mm.	0.588

Figure D.8.

EFFECT OF TEMPERATURE ON OXIDATION PRODUCTS.

Product : FORMALDEHYDE.

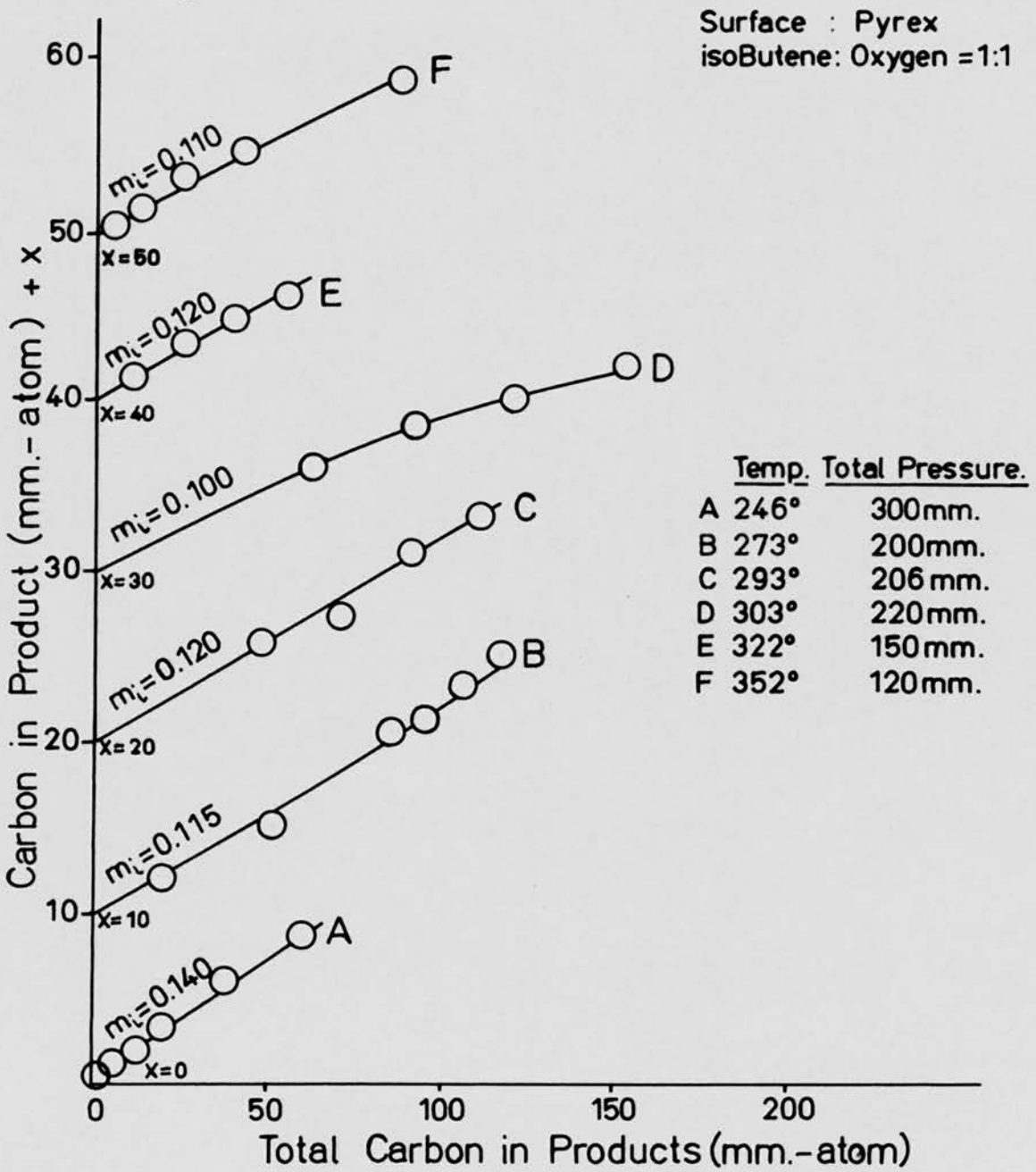


Figure D.9.

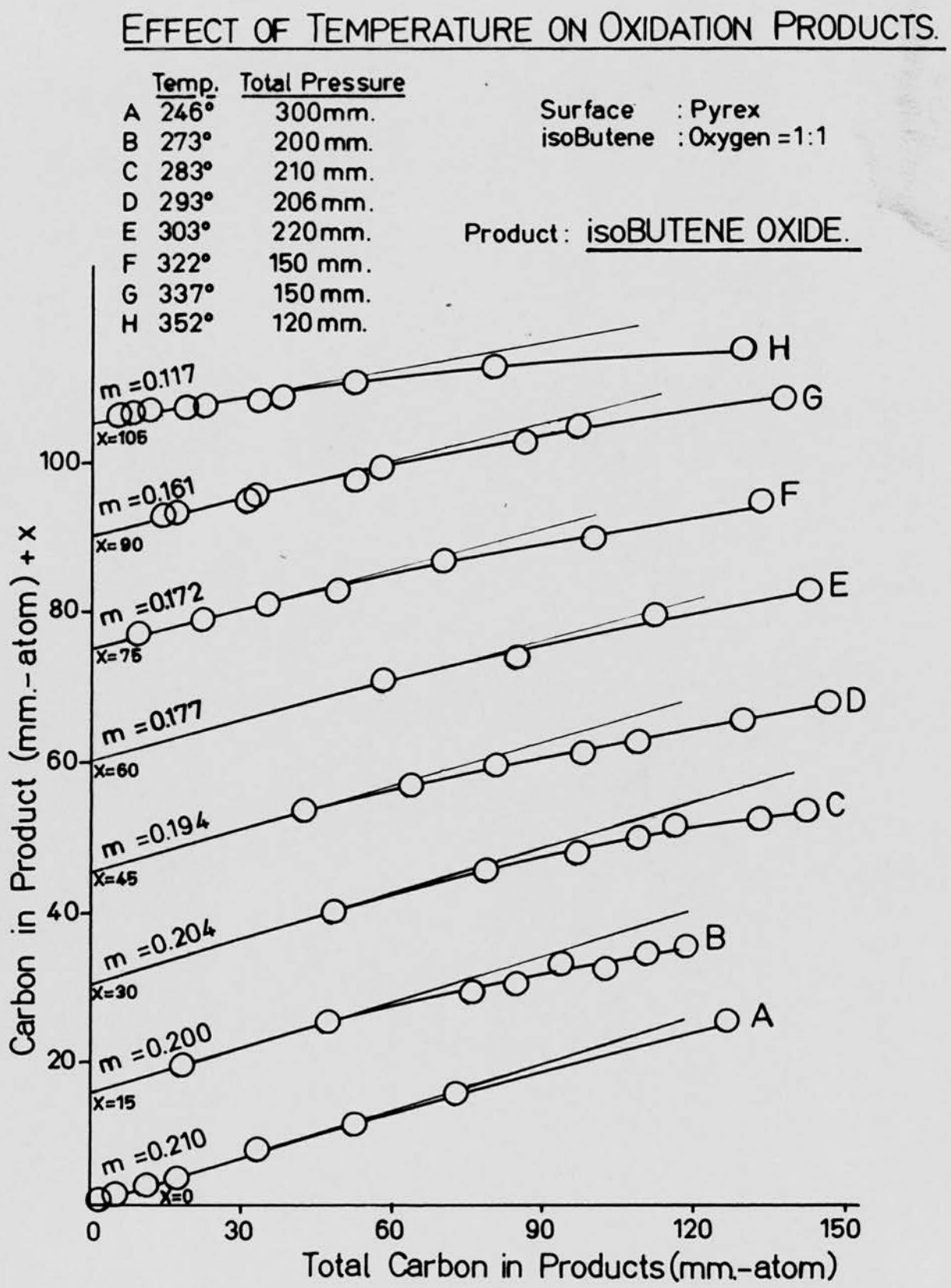

EFFECT OF TEMPERATURE ON OXIDATION PRODUCTS.
Temp. Total Pressure
A 246° 300mm.
B 273° 200mm.
C 283° 210 mm.
D 293° 206mm.
E 303° 220mm.
F 322° 150 mm.
G 337° 150mm.
H 352° 120mm.
Surface : Pyrex
isoButene : Oxygen = 1:1
Product: isoBUTENE OXIDE.
m =0.117
X=105
m =0.161
X=90
m =0.172
X=75
m =0.177
X=60
m =0.194
X=45
m =0.204
X=30
m =0.200
X=15
m =0.210
X=0
H
G
F
E
D
C
B
A
Carbon in Product (mm.-atom) + x
Total Carbon in Products (mm.-atom)
0
30
60
90
120
150
20
40
60
80
100

Figure D.10.

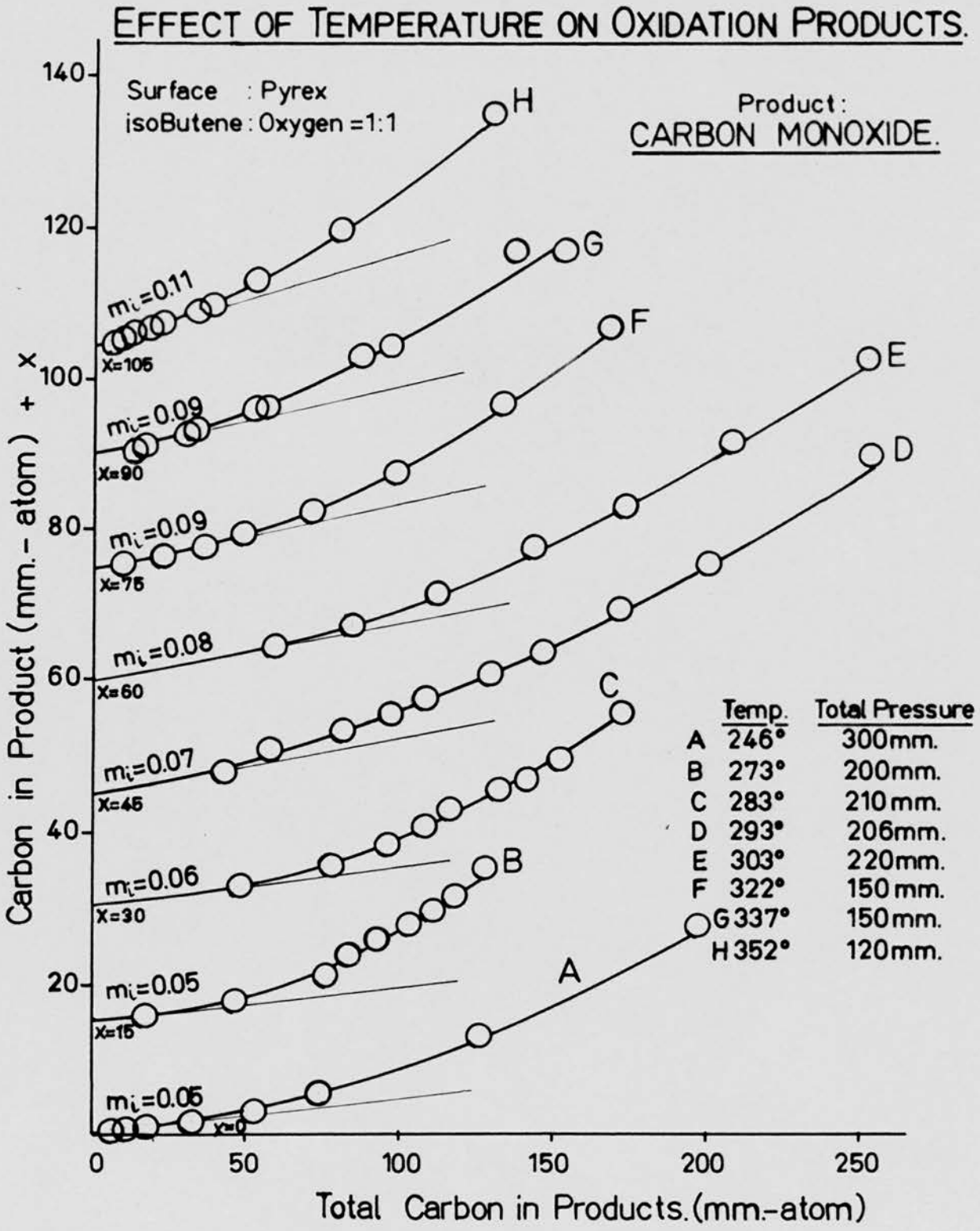

EFFECT OF TEMPERATURE ON OXIDATION PRODUCTS.
Surface : Pyrex
isoButene : Oxygen = 1:1
Product:
CARBON MONOXIDE.
Carbon in Product (mm.- atom) + x
Total Carbon in Products.(mm.-atom)
0
50
100
150
200
250
20
40
60
80
100
120
140
mi=0.11
X=105
mi=0.09
X=90
mi=0.09
X=75
mi=0.08
X=60
mi=0.07
X=45
mi=0.06
X=30
mi=0.05
X=15
mi=0.05
X=0
A
B
C
D
E
F
G
H
Temp.
Total Pressure
A 246° 300mm.
B 273° 200mm.
C 283° 210mm.
D 293° 206mm.
E 303° 220mm.
F 322° 150mm.
G 337° 150mm.
H 352° 120mm.

Figure D.11.

EFFECT OF TEMPERATURE ON OXIDATION PRODUCTS.

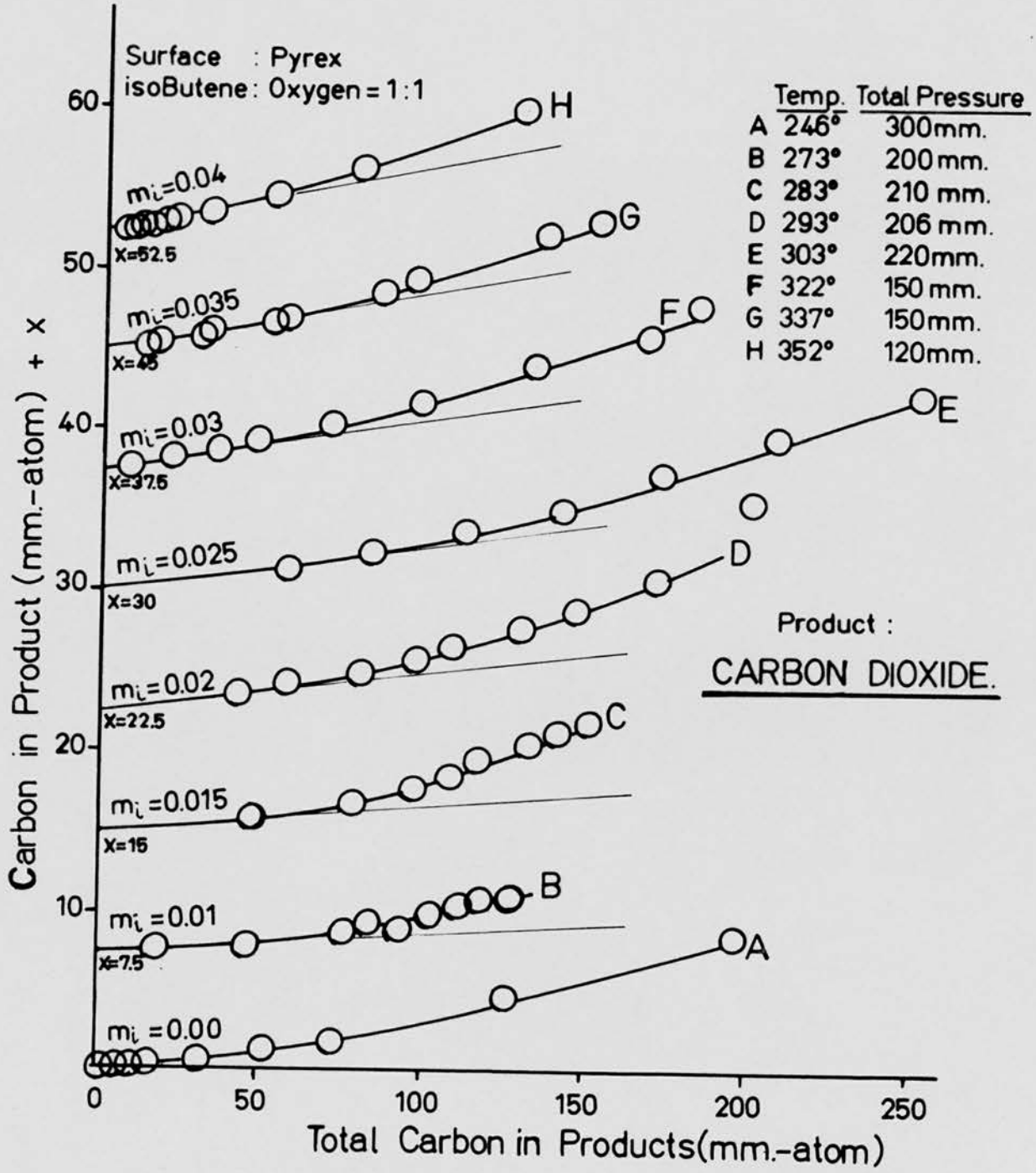


Figure D. 12.

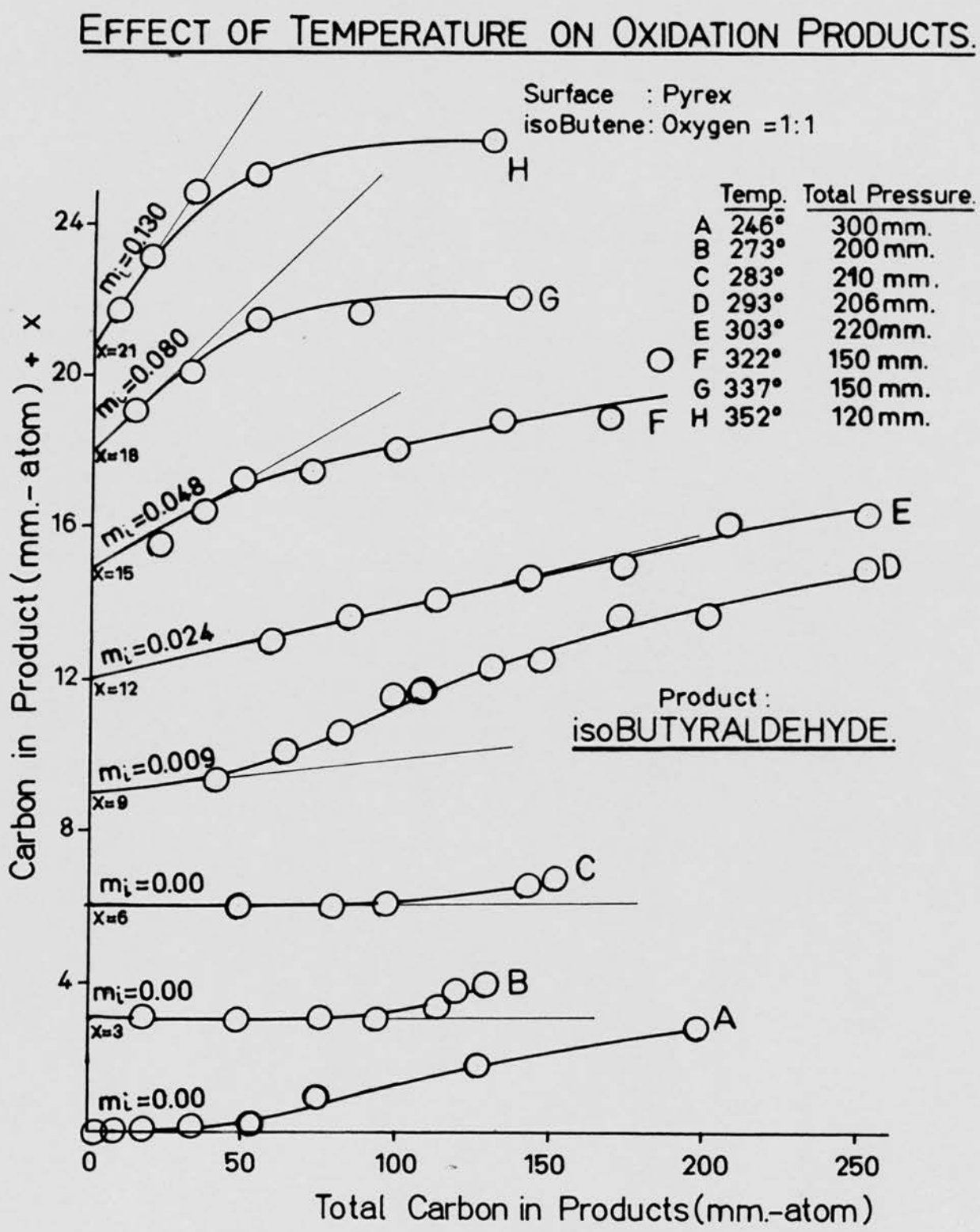

EFFECT OF TEMPERATURE ON OXIDATION PRODUCTS.
Surface : Pyrex
isoButene: Oxygen =1:1
Temp. Total Pressure.
A 246° 300mm.
B 273° 200mm.
C 283° 210 mm.
D 293° 206mm.
E 303° 220mm.
F 322° 150 mm.
G 337° 150 mm.
H 352° 120mm.
Product :
isoBUTYRALDEHYDE.
Carbon in Product (mm.-atom) + x
Total Carbon in Products (mm.-atom)
mi=0.130
x=21
mi=0.080
x=18
mi=0.048
x=15
mi=0.024
x=12
mi=0.009
x=9
mi=0.00
x=6
mi=0.00
x=3
mi=0.00
0
50
100
150
200
250
4
8
12
16
20
24
A
B
C
D
E
F
G
H

Figure D.13.

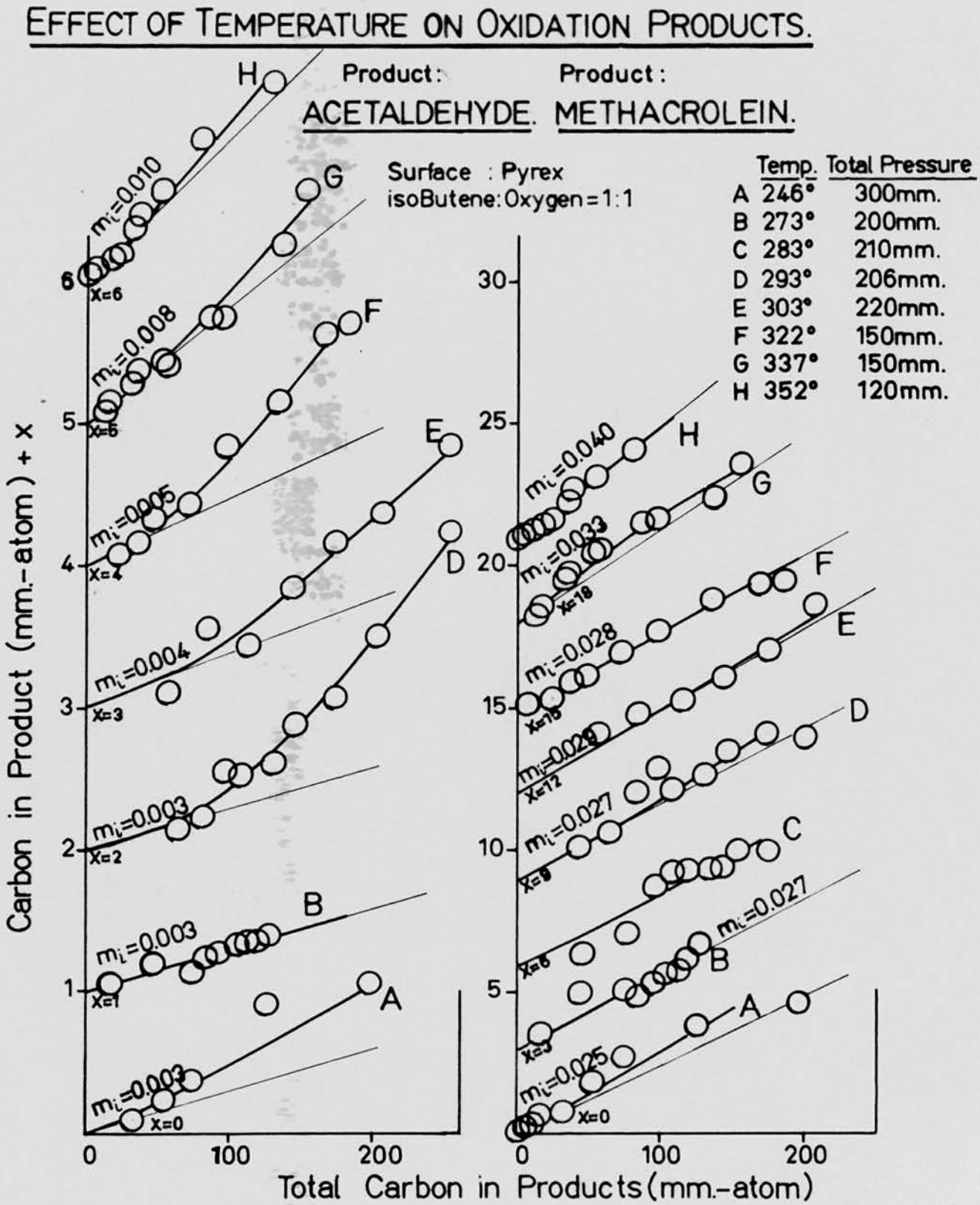
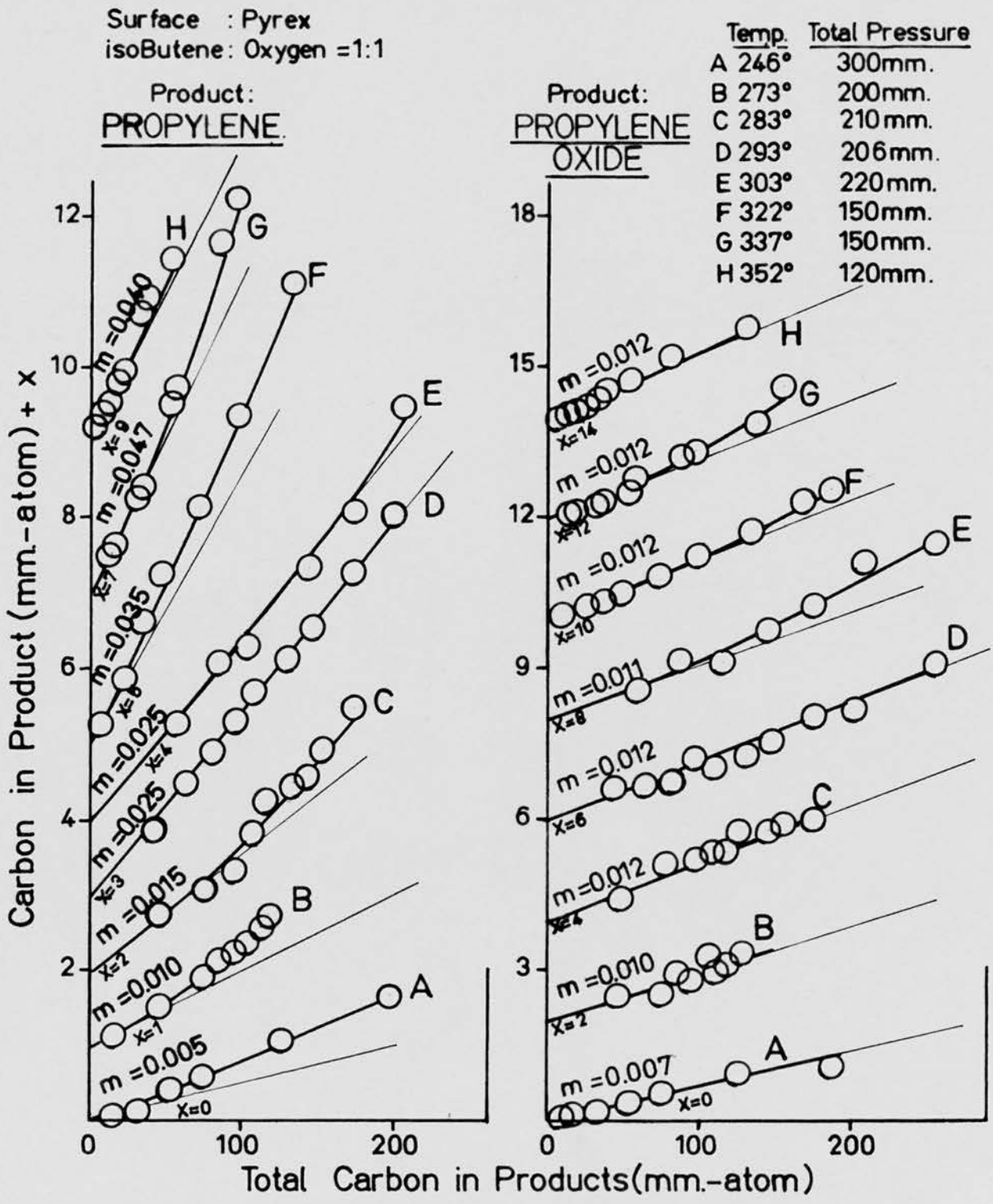

EFFECT OF TEMPERATURE ON OXIDATION PRODUCTS.
Product: ACETALDEHYDE.
Product: METHACROLEIN.
Surface : Pyrex
isoButene: Oxygen = 1:1
Temp. Total Pressure
A 246° 300mm.
B 273° 200mm.
C 283° 210mm.
D 293° 206mm.
E 303° 220mm.
F 322° 150mm.
G 337° 150mm.
H 352° 120mm.
Carbon in Product (mm.-atom) + x
Total Carbon in Products (mm.-atom)
0
100
200
1
2
3
4
5
6
10
15
20
25
30
m_i=0.010
m_i=0.008
m_i=0.005
m_i=0.004
m_i=0.003
m_i=0.003
m_i=0.003
m_i=0.040
m_i=0.033
m_i=0.028
m_i=0.027
m_i=0.027
m_i=0.025
X=6
X=5
X=4
X=3
X=2
X=1
X=0
X=15
X=12
X=9
X=6
X=3
X=0
A
B
C
D
E
F
G
H

Figure D.14.

EFFECT OF TEMPERATURE ON OXIDATION PRODUCTS.



1.3. The effect of surface and inert gas.

Figures D.15 - D.28 represent the effect on the initial yields of products of varying the nature of the reaction vessel surface.

The results from runs carried out in a boric acid coated vessel are given for each product in Figures D.15 - D.17, and a comparison graph of the initial gradients of each product, in each of the three runs in the boric acid vessel and in the corresponding run in a clean pyrex vessel, is given in Figure D.18. The curves marked A, B and C, are comprised of analytical results from Oxidations 14, 15 and 16.

The results from runs using a potassium chloride coated vessel are presented in a similar way in Figures D.19 - D.22, where curves A, B and C are comprised of analytical results from Oxidations Nos. 17, 18 and 19.

Similarly the results from runs in a sodium hydroxide coated vessel are presented in Figures D.23 - D.25. Figure D.26 represents the effect of added inert gas on the initial yields of products in the sodium hydroxide coated vessel. In Figure D.27 a comparison of all the initial product yields in the sodium hydroxide coated vessel, including the run with nitrogen added, is made with the corresponding results in the clean pyrex vessel.

Figure D.28 gives a composite comparison of the initial yields of products from runs in a clean pyrex vessel, and in 'aged' boric acid, potassium chloride and sodium hydroxide coated vessels.

Figure D. 15.

EFFECT OF SURFACE ON OXIDATION PRODUCTS.

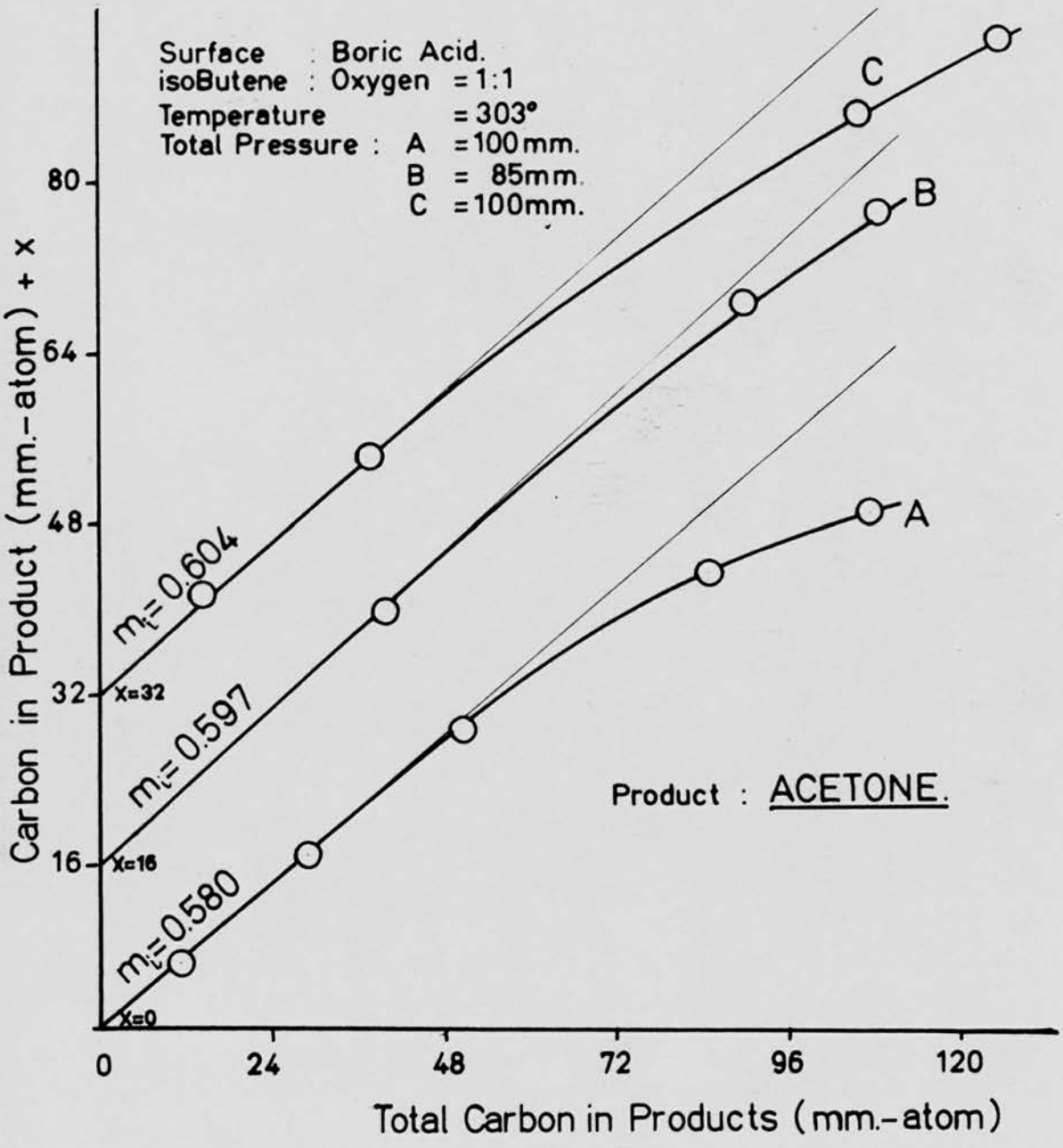


Figure D.16.

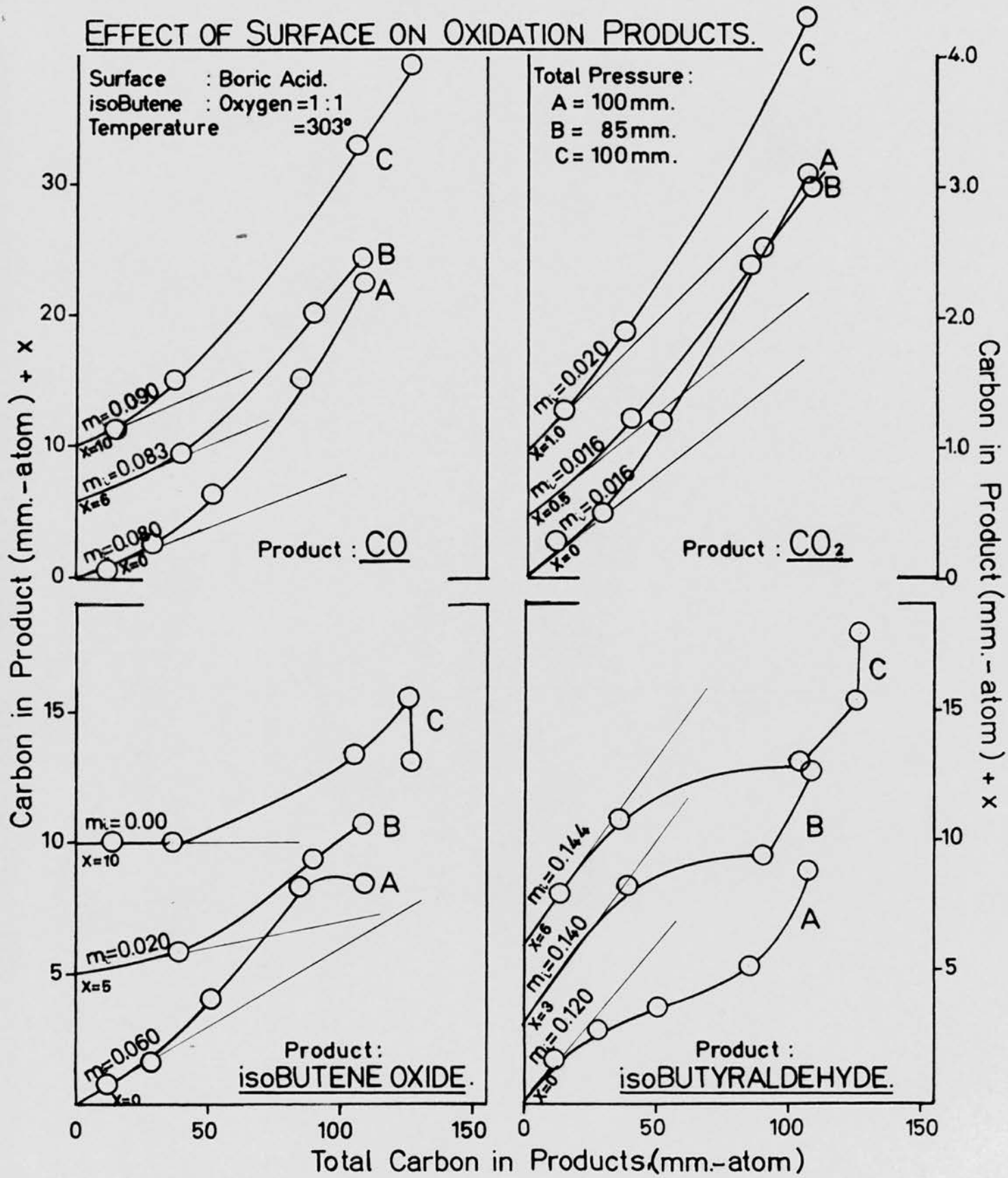

EFFECT OF SURFACE ON OXIDATION PRODUCTS.
Surface : Boric Acid.
isoButene : Oxygen = 1 : 1
Temperature = 303°
Total Pressure:
A = 100 mm.
B = 85 mm.
C = 100 mm.
Product : CO
Product : CO2
Product: isoBUTENE OXIDE.
Product : isoBUTYRALDEHYDE.
Carbon in Product (mm.-atom) + x
Carbon in Product (mm.-atom) + x
Total Carbon in Products (mm.-atom)
0
50
100
150
0
5
10
15
20
30
0
1.0
2.0
3.0
4.0
A
B
C
mi=0.090
x=10
mi=0.083
x=6
mi=0.080
x=0
mi=0.020
x=1.0
mi=0.016
x=0.5
mi=0.016
x=0
mi=0.00
x=10
mi=0.020
x=5
mi=0.060
x=0
mi=0.144
x=6
mi=0.140
x=3
mi=0.120
x=0

Figure D.17.

EFFECT OF SURFACE ON OXIDATION PRODUCTS.

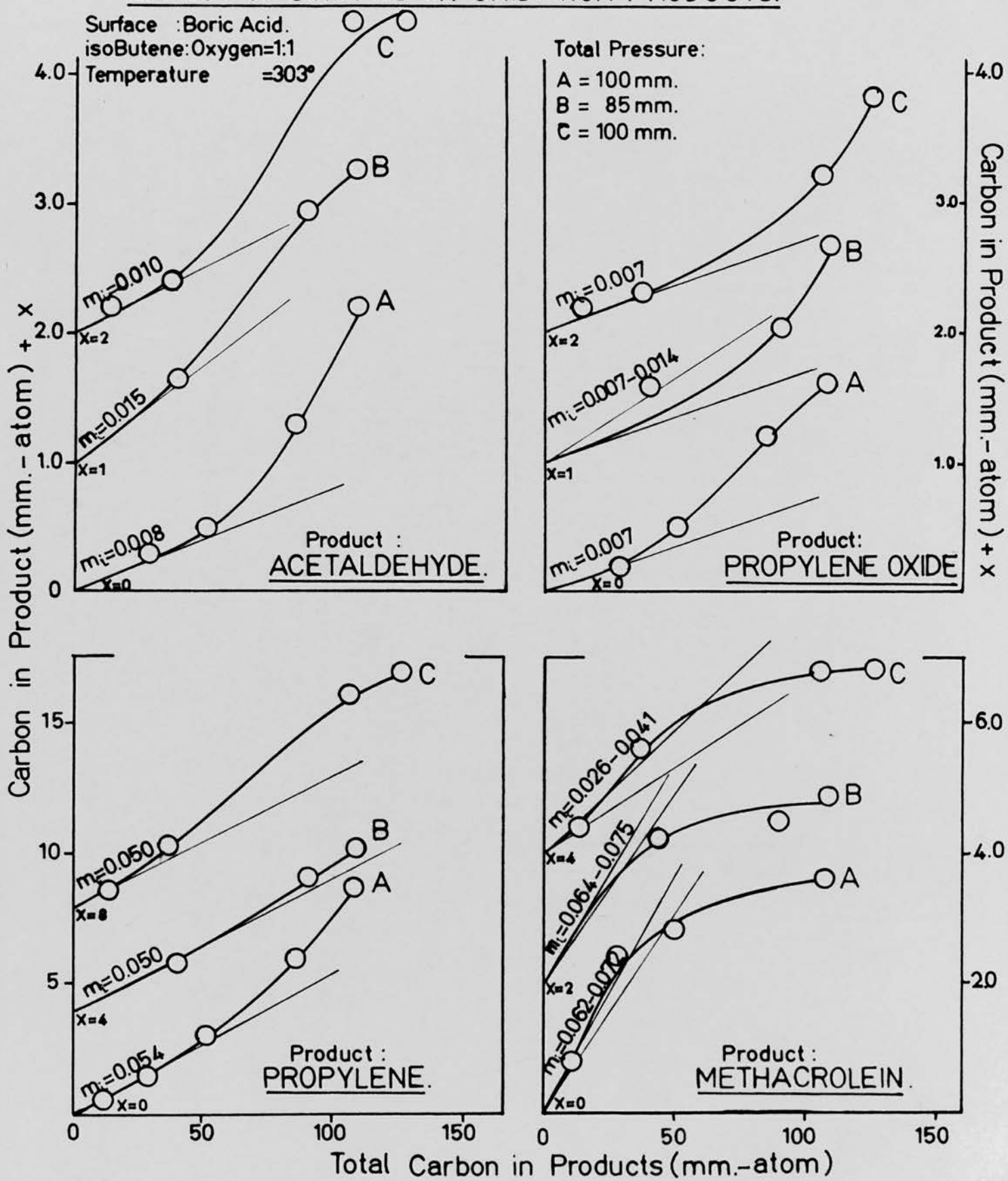


Figure D.18.

EFFECT OF SURFACE ON OXIDATION PRODUCTS.

Surface : Boric Acid.
isoButene : Oxygen = 1:1
Temperature = 303°

Total Pressure
Clean Pyrex = 200mm.
Boric Acid RunA = 100mm.
RunB = 85mm.
RunC = 100mm.

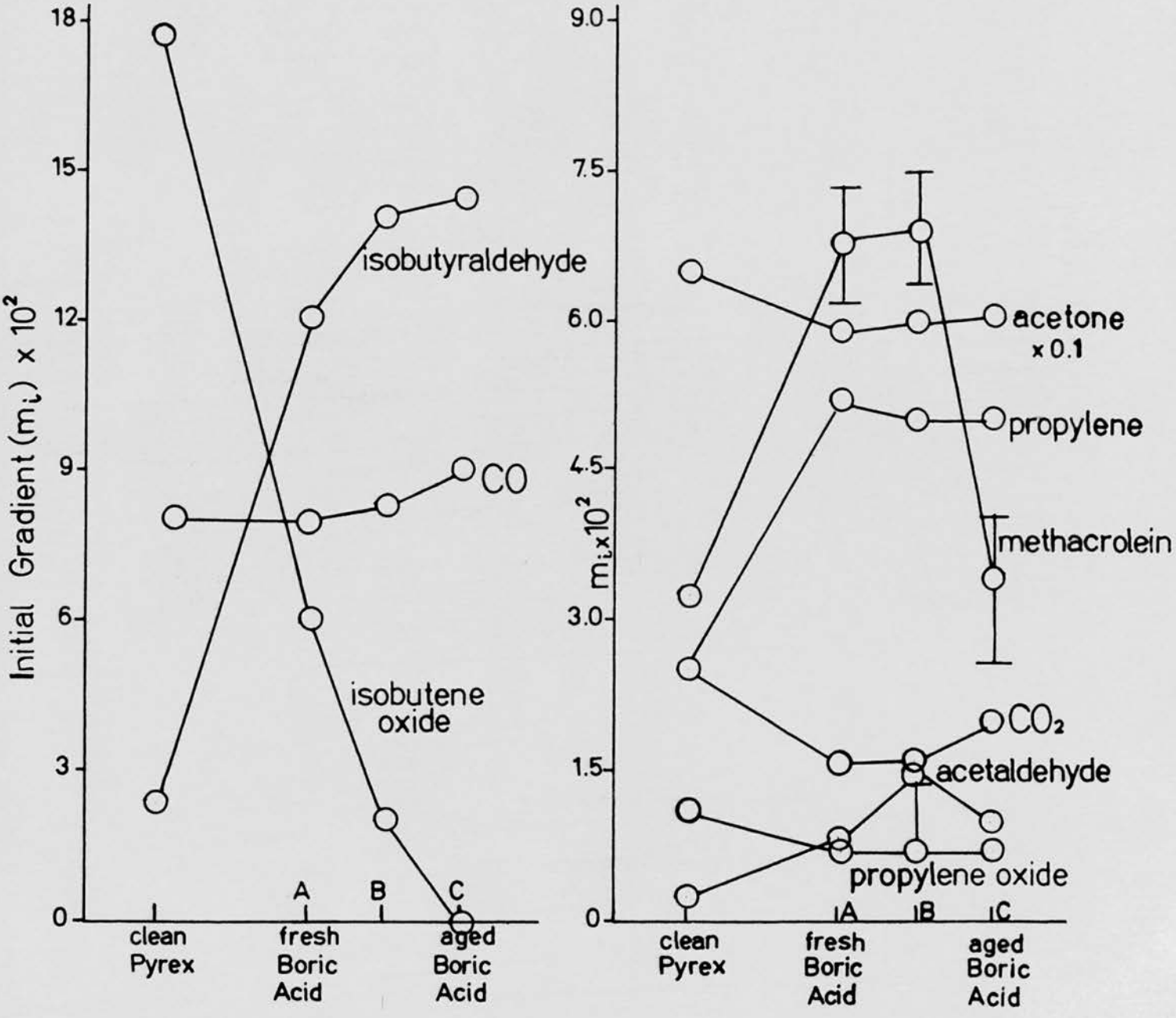


Figure D.19.

EFFECT OF SURFACE ON OXIDATION PRODUCTS.

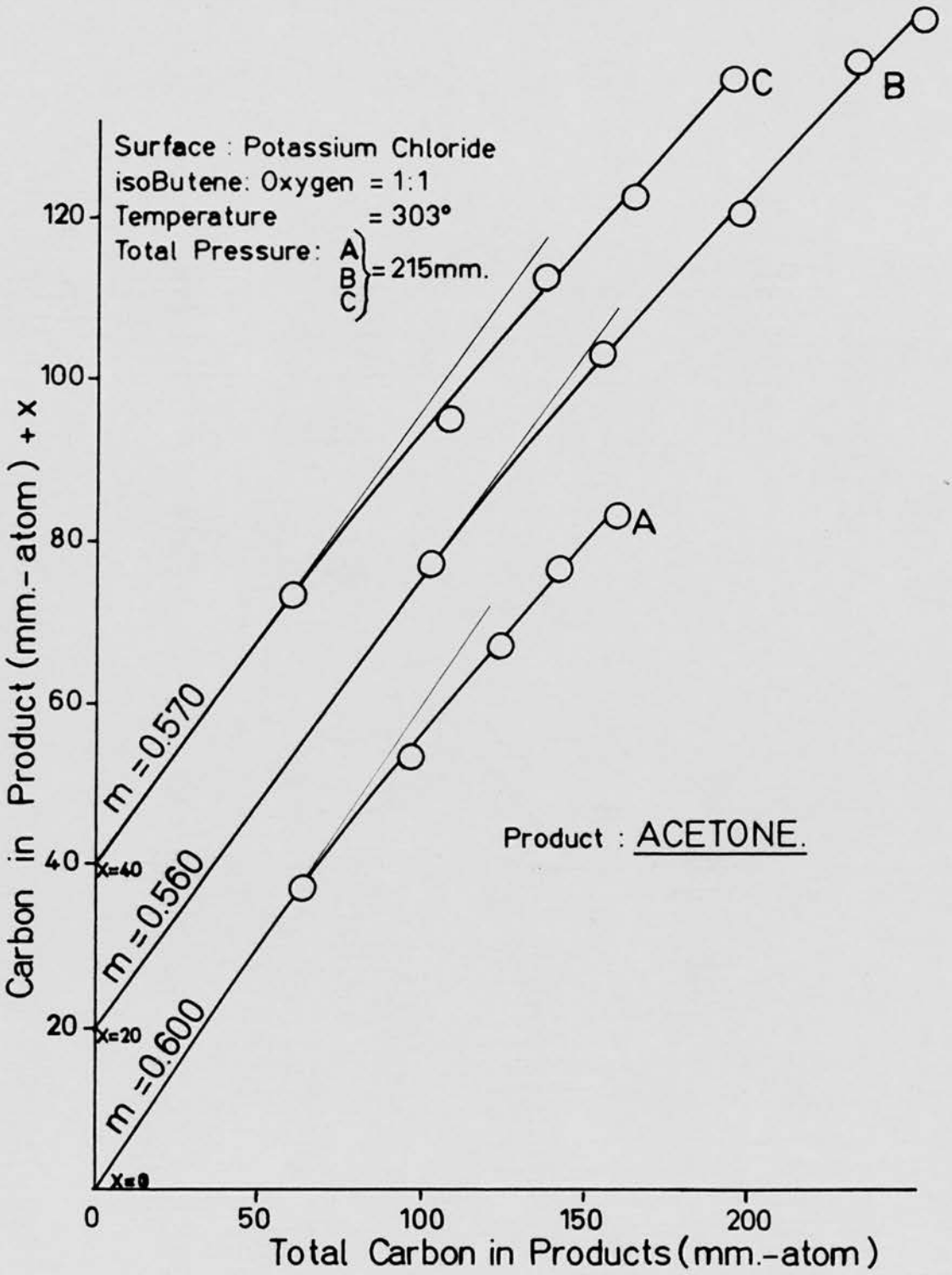


Figure D. 20.

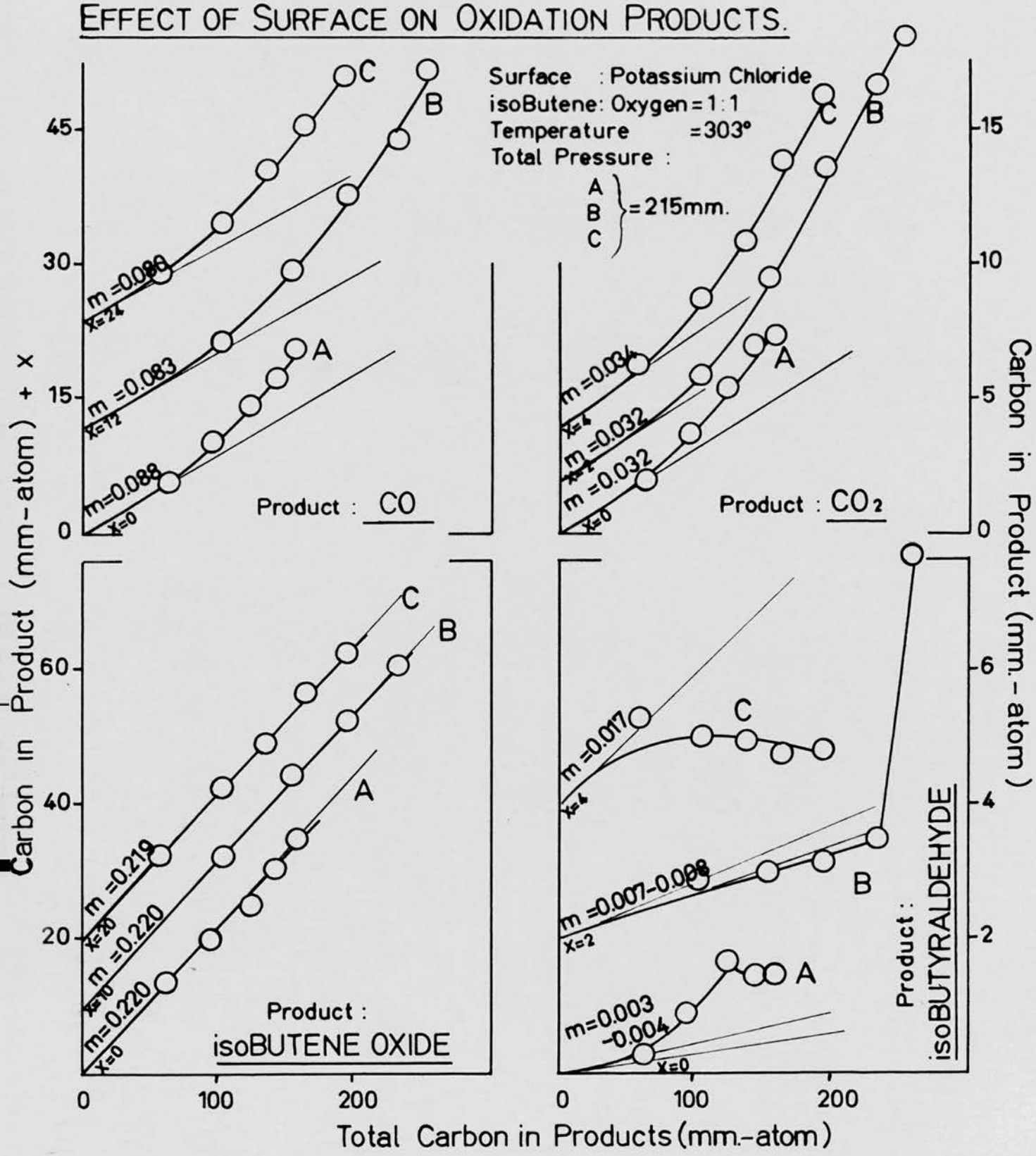

EFFECT OF SURFACE ON OXIDATION PRODUCTS.
Surface : Potassium Chloride
isoButene: Oxygen = 1:1
Temperature =303°
Total Pressure :
A
B
C
} = 215mm.
Product : CO
Product : CO2
Product : isoBUTENE OXIDE
Product : isoBUTYRALDEHYDE
m =0.088
x=24
m =0.083
x=12
m=0.088
x=0
m =0.034
x=4
m =0.032
x=2
m =0.032
x=0
m =0.219
x=20
m =0.220
x=10
m=0.220
x=0
m =0.017
x=4
m =0.007-0.008
x=2
m=0.003
-0.004
x=0
Carbon in Product (mm-atom) + x
Carbon in Product (mm.-atom)
Total Carbon in Products (mm.-atom)
0
15
30
45
5
10
20
40
60
100
200
2
4
6

Figure D.21.

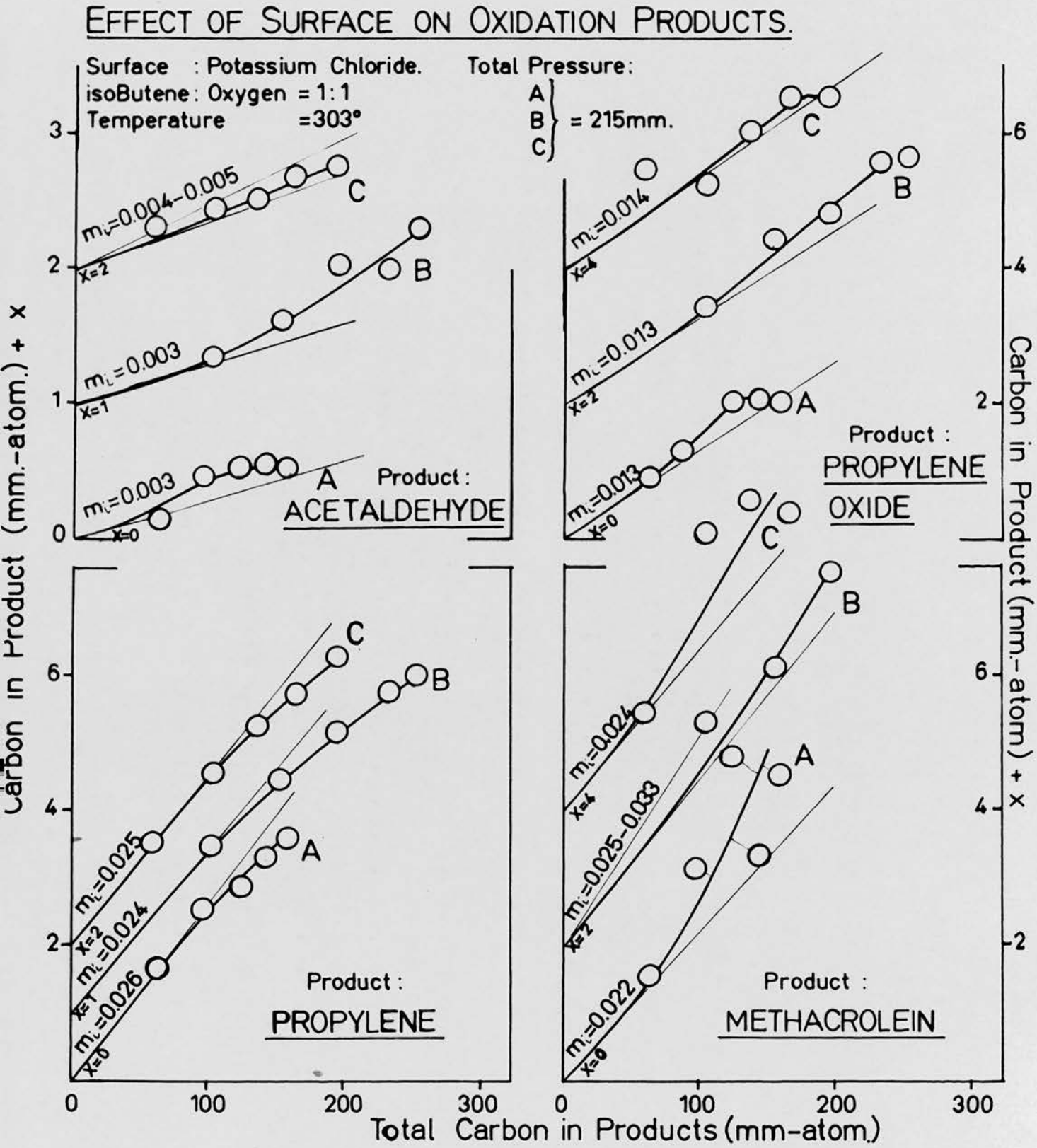

EFFECT OF SURFACE ON OXIDATION PRODUCTS.
Surface : Potassium Chloride.
isoButene : Oxygen = 1:1
Temperature =303°
Total Pressure:
A
B
C
= 215mm.
Product :
ACETALDEHYDE
Product :
PROPYLENE OXIDE
Product :
PROPYLENE
Product :
METHACROLEIN
Carbon in Product (mm.-atom.) + x
Carbon in Product (mm.-atom) + x
Total Carbon in Products (mm-atom.)
0
100
200
300
2
4
6

Figure D.22.

EFFECT OF SURFACE ON OXIDATION PRODUCTS.

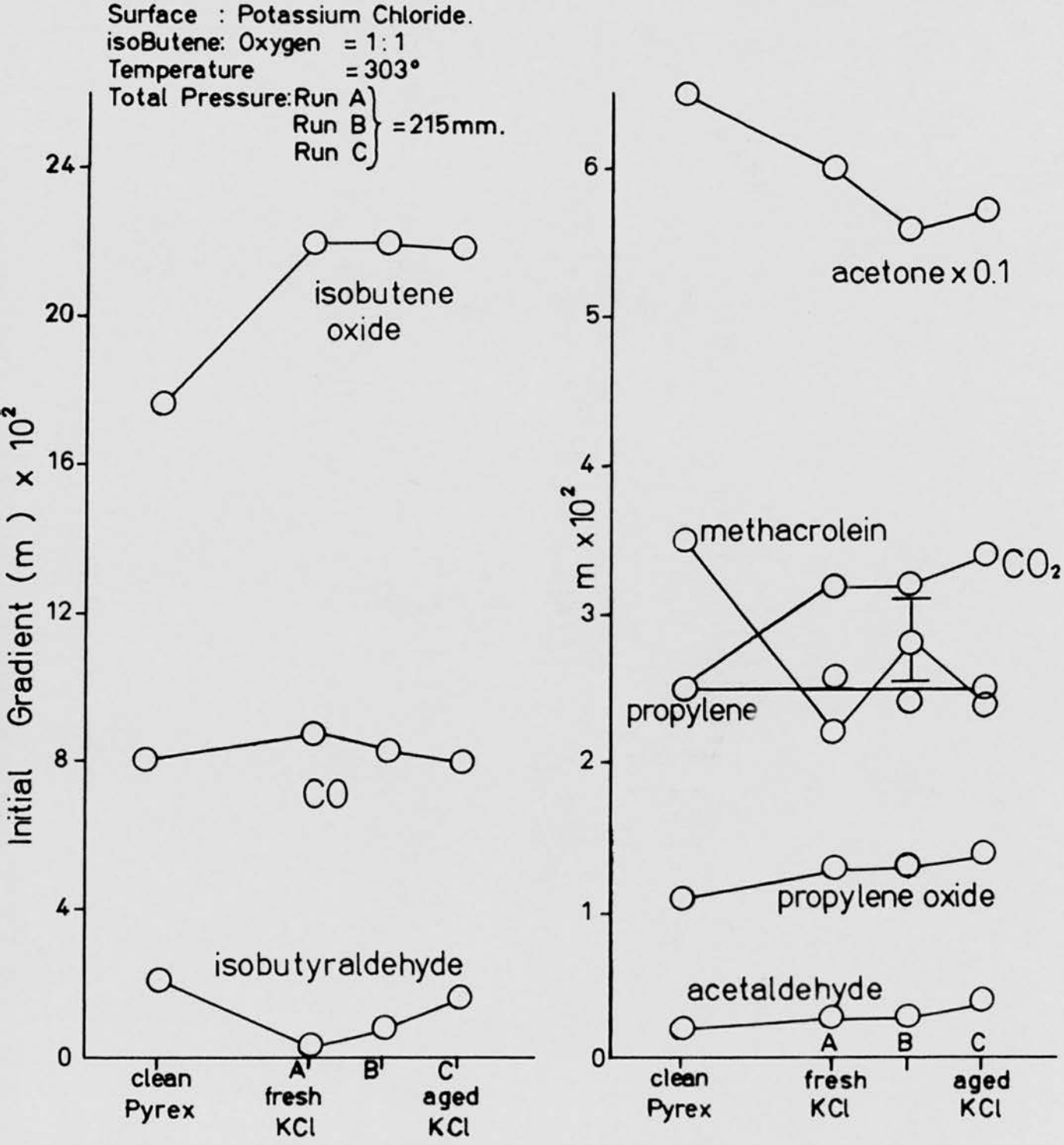


Figure D.23.

EFFECT OF SURFACE ON OXIDATION PRODUCTS.

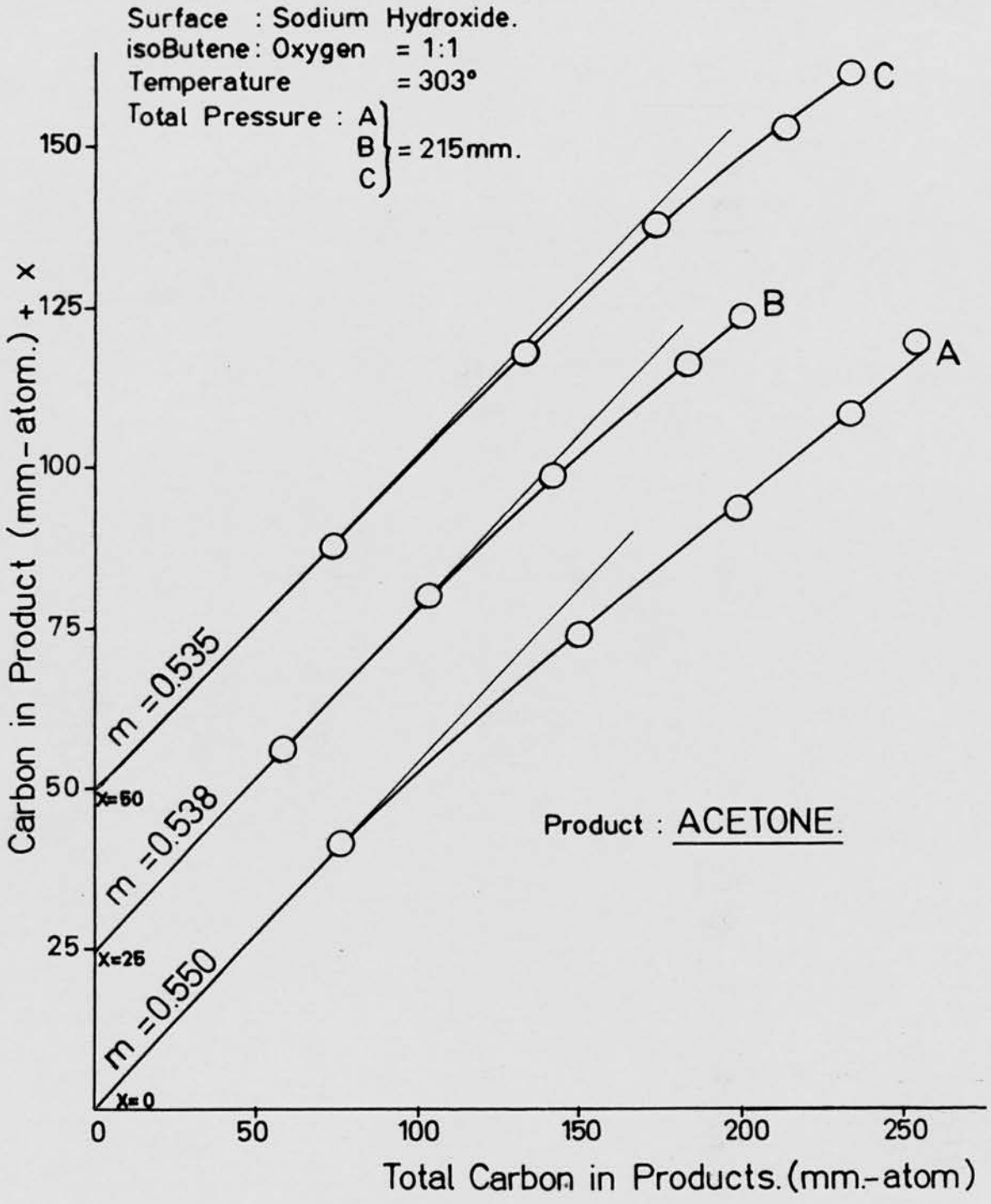


Figure D. 24.

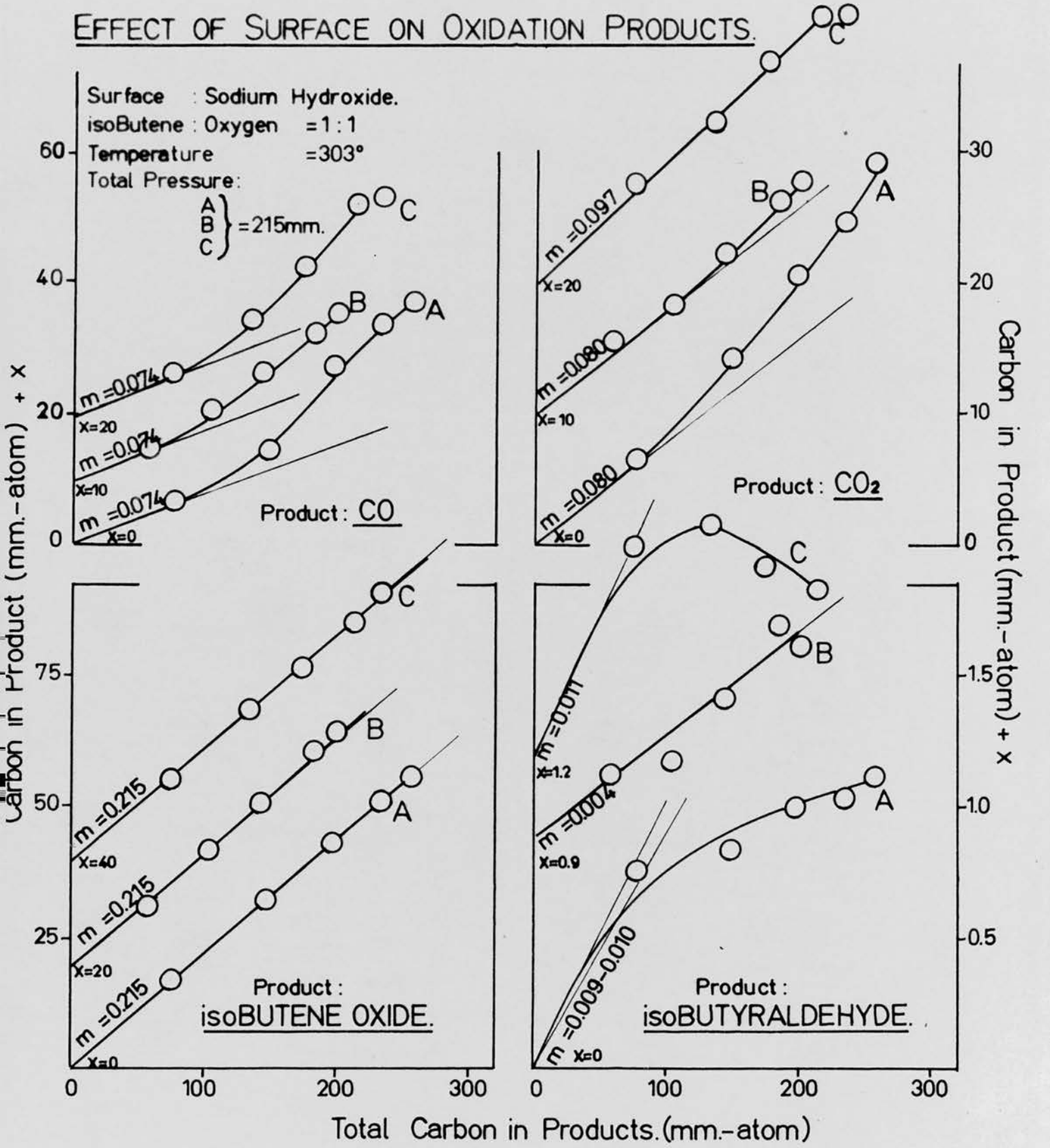

EFFECT OF SURFACE ON OXIDATION PRODUCTS.
Surface : Sodium Hydroxide.
isoButene : Oxygen =1 : 1
Temperature =303°
Total Pressure:
A
B
C
=215mm.
Product : CO
Product : CO2
Product :
isoBUTENE OXIDE.
Product :
isoBUTYRALDEHYDE.
Carbon in Product (mm.-atom) + x
Carbon in Product (mm.-atom) + x
Total Carbon in Products.(mm.-atom)

Figure D. 25.

EFFECT OF SURFACE ON OXIDATION PRODUCTS.

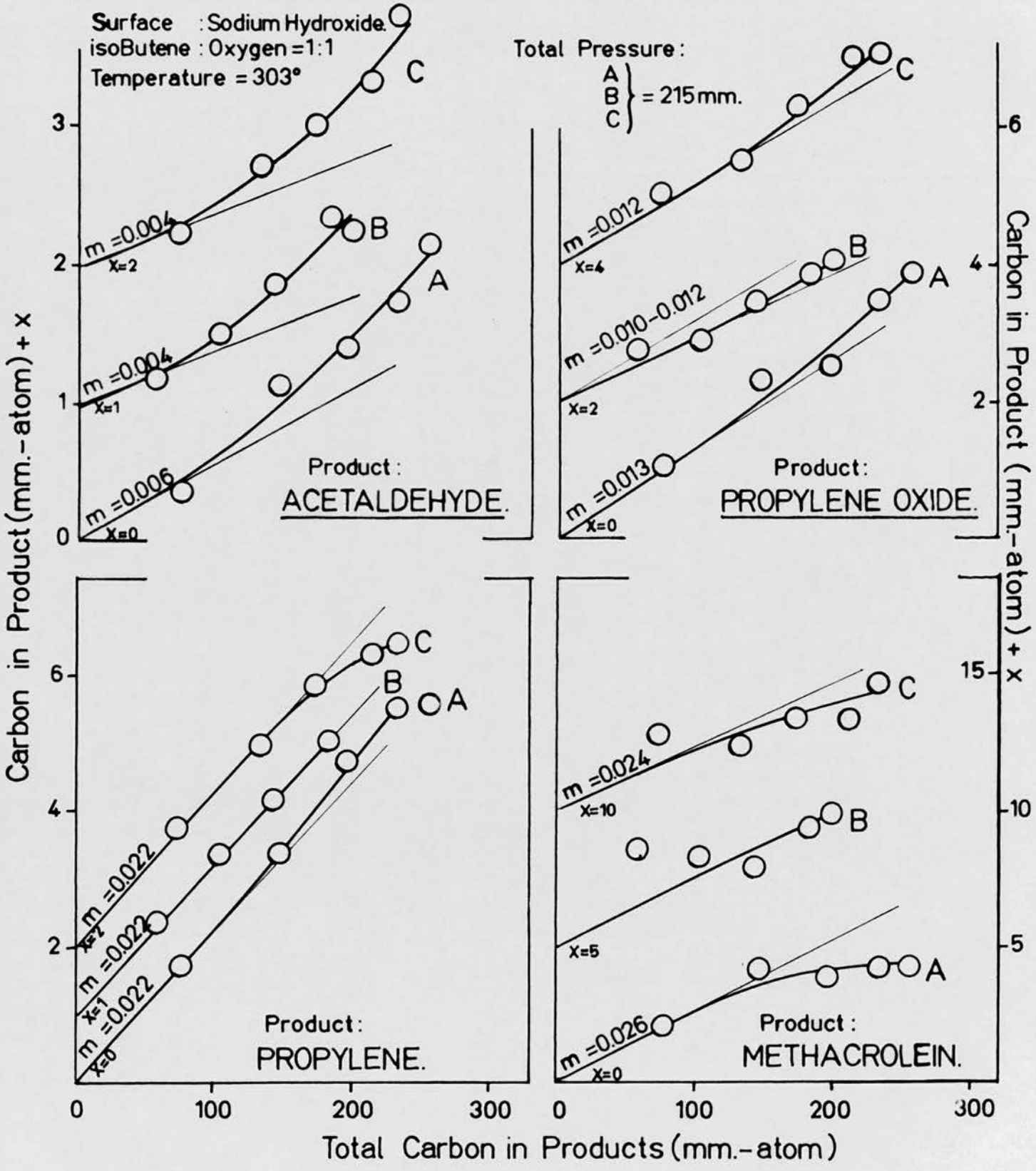


Figure D.26.

EFFECT OF INERT GAS ON OXIDATION PRODUCTS.

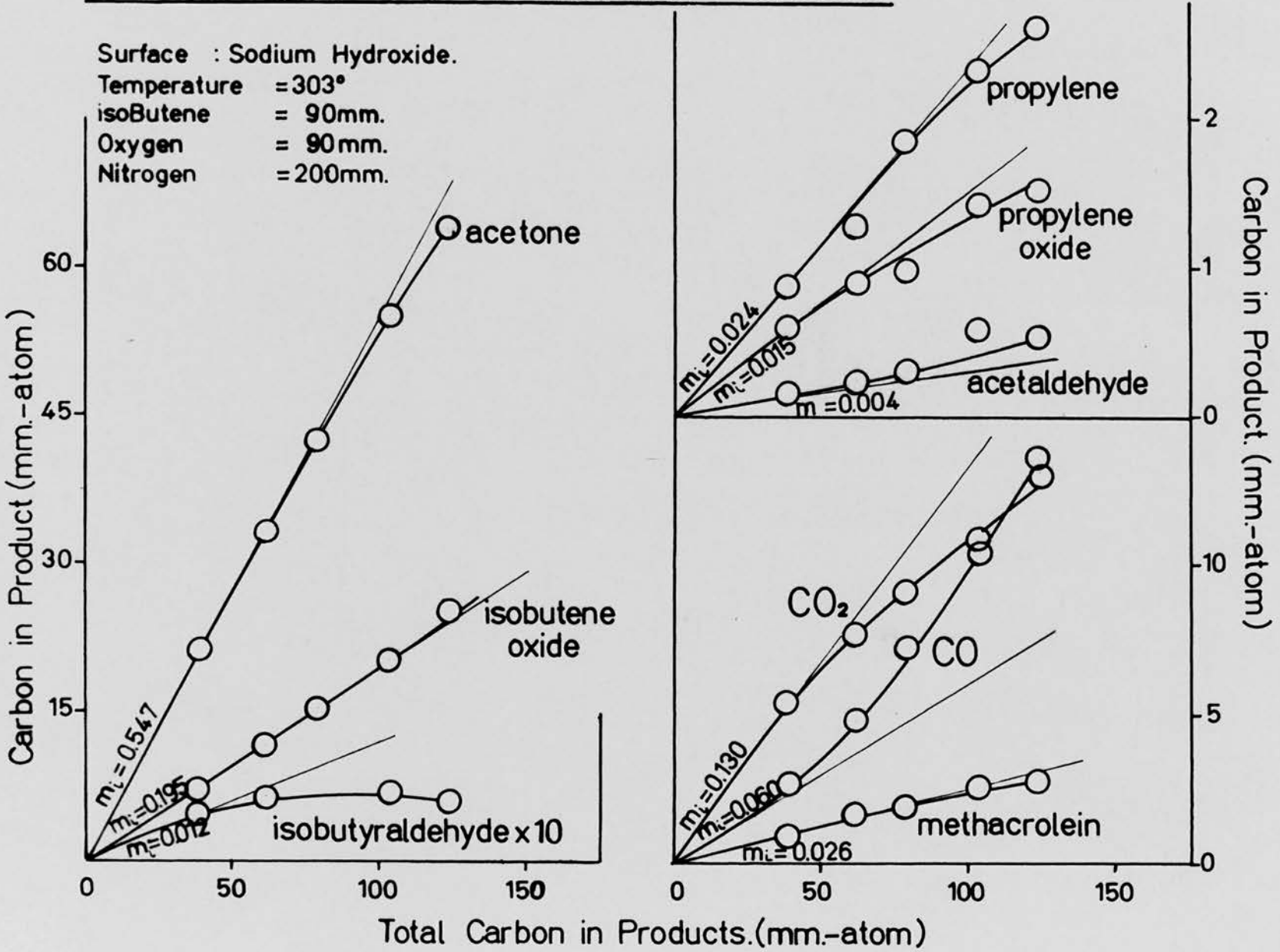


Figure D.27.

EFFECT OF SURFACE AND INERT GAS ON OXIDATION PRODUCTS.

Surface : Sodium Hydroxide.
Temperature = 303°
isoButene : Oxygen = 1:1

Run:	N_2 added	Total Pressure
A	0	200mm.
B	0	215mm.
C	0	215mm.
D	0	215mm.
E	200mm.	380mm.

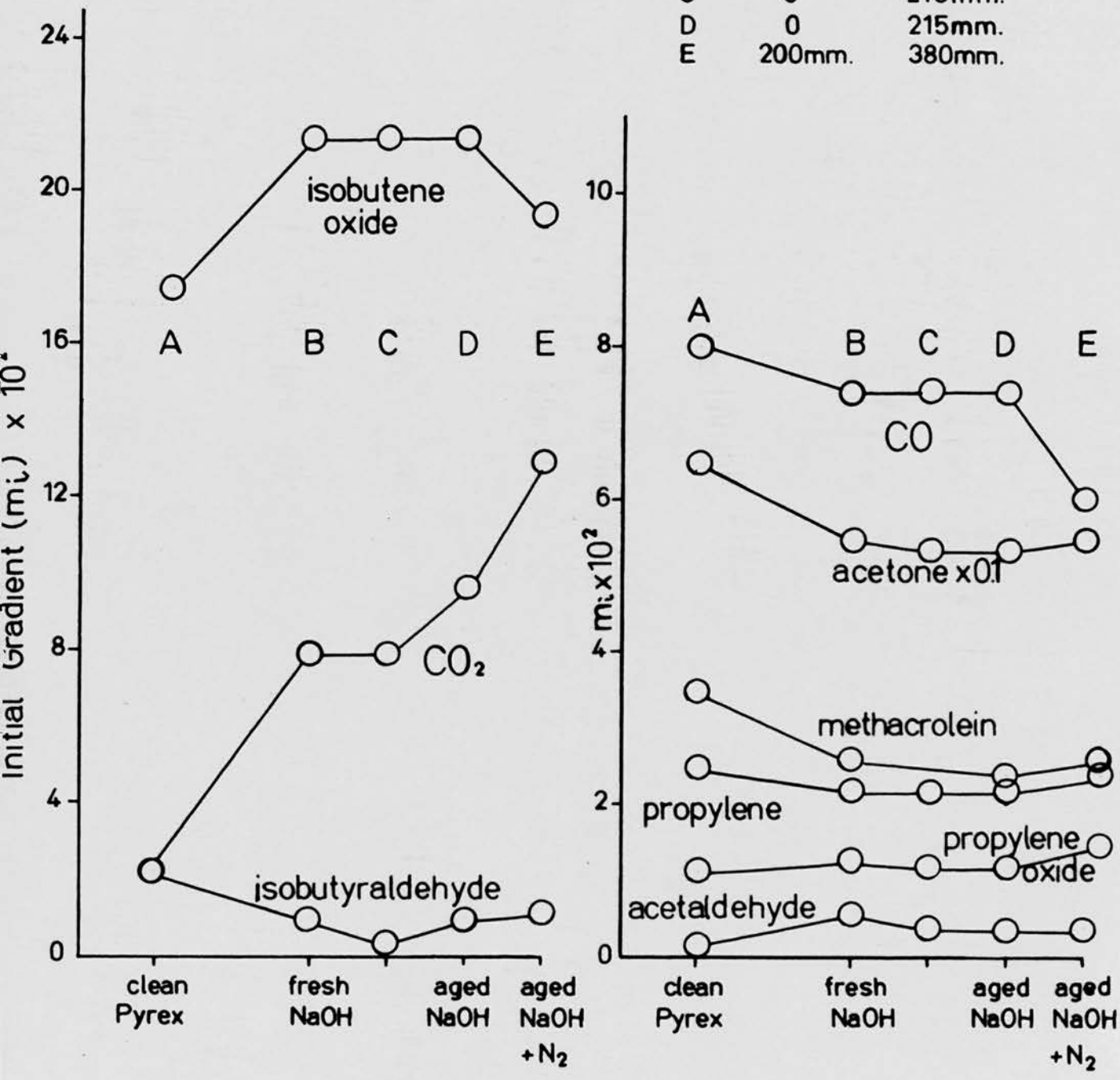
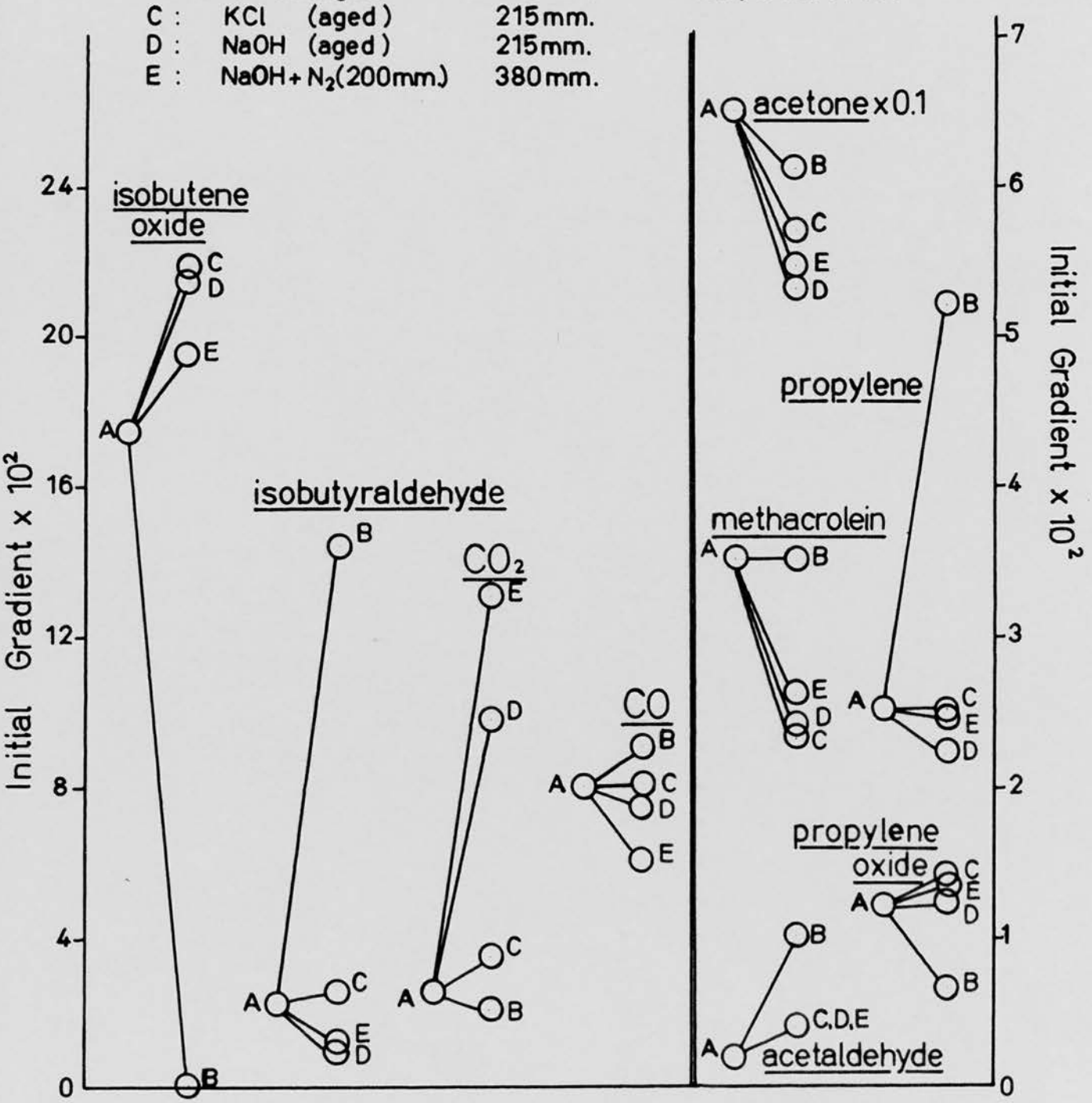


Figure D.28.

EFFECT OF SURFACE ON OXIDATION PRODUCTS.

Run :	Total Pressure
A : Clean aged Pyrex	220mm.
B : Boric Acid (aged)	100mm.
C : KCl (aged)	215mm.
D : NaOH (aged)	215mm.
E : NaOH + N_2 (200mm.)	380mm.

isoButene : Oxygen = 1:1
Temperature : 303°



2. Initial % molar yields of products

From the values of the initial gradients obtained in the previous section the initial % molar yields of all the products (including formaldehyde) were calculated for the oxidations in which formaldehyde was analysed.

The effect of reactant composition, (Oxidations 1 - 5), on initial % molar yield is given in Table D.1., Figure D.29. The effect of temperature, (Oxidations 1, 8 - 10, 12, 13), is given in Table D.2., Figure D.30., and of surface variation (Oxidations 16, 19 and 22), in Table D.3., Figures D.31., D.32.

TABLE No.D.1. (figure D.29)

Percentage molar yields of products in the initial stages.

Temperature = 273°

Oxidation Number	1	2	3	4	5
isoButene : Oxygen	1:1	1:2	2:1	1:2	2:1
Total Press. (mm.Hg.)	200	318	150	150	300
Acetone	43.9	46.5	42.9	41.4	39.8
Formaldehyde	24.4	22.9	23.0	26.7	21.0
IsoButene Oxide	9.3	9.9	10.0	7.6	11.4
Carbon Monoxide	9.3	8.7	10.0	9.6	11.4
Carbon Dioxide	1.9	1.5	0.8	2.0	1.3
Propylene	0.6	0.4	1.3	0.6	1.1
Methacrolein	1.2	0.5	0.8	1.2	1.7
Propylene Oxide	0.6	0.4			0.8
Acetaldehyde	0.3	0.4			0.2
Water	8.5	8.8	11.2	11.1	11.4

Figure D.29.

EFFECT OF REACTANT COMPOSITION ON INITIAL YIELDS.

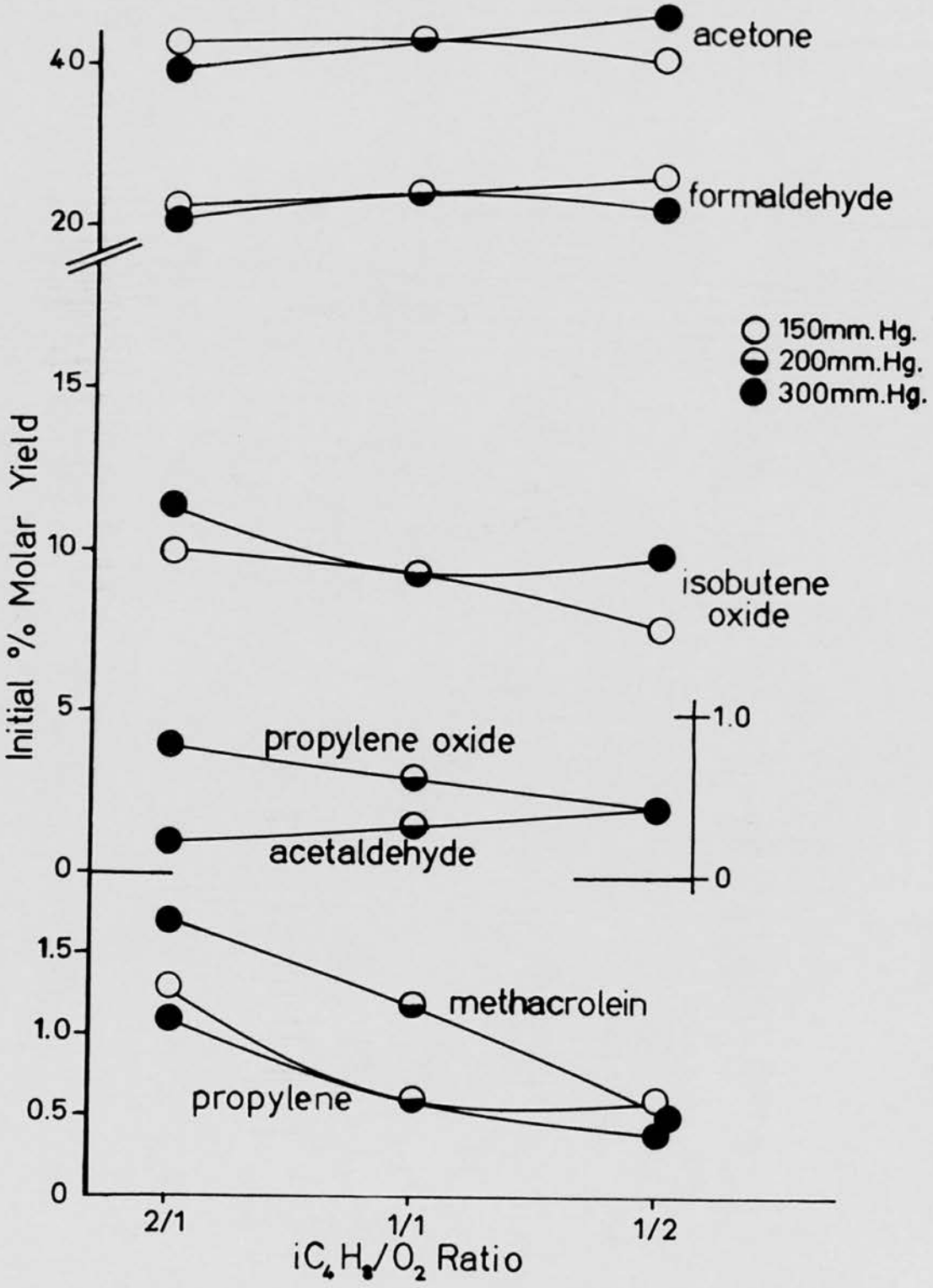


TABLE No.D.2. (figure D.30.)

Percentage molar yields of products in the initial stages.

Ratio isoButene : oxygen = 1 : 1

Oxidation Number	13	1	8	9	10	12
Temperature	246°	273°	293°	303°	322°	352°
Total Press (mm.Hg.)	300	200	206	220	150	120
Acetone	41.6	43.9	36.9	37.0	32.1	29.3
Formaldehyde	28.2	24.4	22.8	19.0	20.8	18.4
isoButene Oxide	9.1	9.3	8.2	7.6	6.6	4.4
isoButyraldehyde	0.0	0.0	0.4	1.0	1.8	4.9
Carbon Monoxide	8.7	9.3	11.7	13.7	13.7	16.4
Carbon Dioxide	0.0	1.9	3.4	4.3	4.5	6.0
Propylene	0.2	0.6	1.3	1.4	1.7	2.0
Methacrolein	1.0	1.2	1.1	1.2	1.0	1.5
Propylene Oxide	0.4	0.6	0.8	0.6	0.7	0.6
Acetaldehyde	0.2	0.3	0.2	0.4	0.4	0.8
Water	10.5	8.5	13.3	13.7	16.8	15.7

Figure D.30.

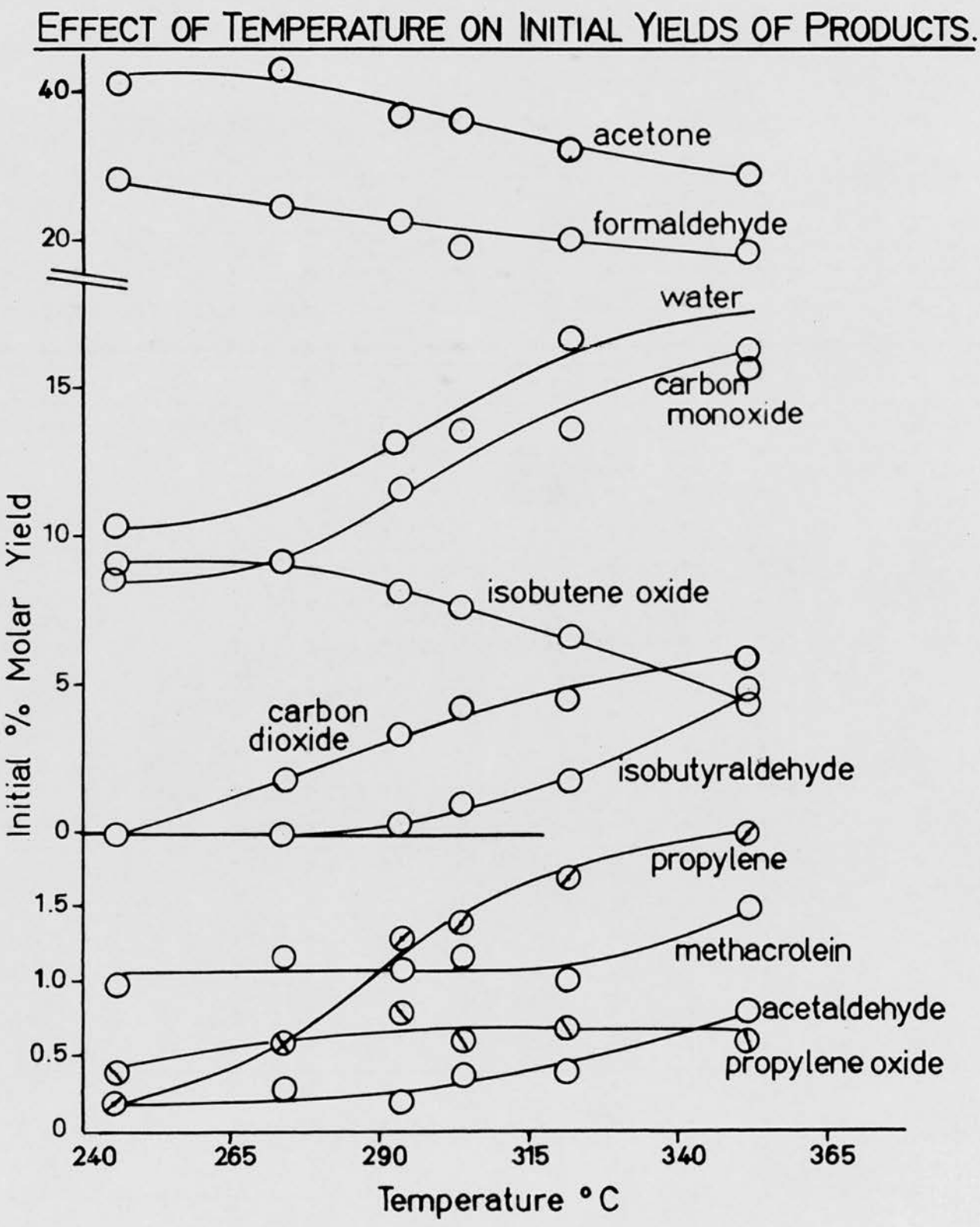

EFFECT OF TEMPERATURE ON INITIAL YIELDS OF PRODUCTS.
Initial % Molar Yield
40
20
15
10
5
0
1.5
1.0
0.5
0
240
265
290
315
340
365
Temperature °C
acetone
formaldehyde
water
carbon monoxide
isobutene oxide
carbon dioxide
isobutyraldehyde
propylene
methacrolein
acetaldehyde
propylene oxide

TABLE No.D.3. (figures D.31. D.32)

Percentage molar yields of products in the initial stages

Ratio isoButene : oxygen = 1 : 1

Temperature = 303°

Oxidation Number	16	19	22
Surface	Boric Acid	KCl	NaOH
Total Press (mm.Hg.)	100	215	215
Acetone	30.6	32.6	30.7
Formaldehyde	27.0	21.2	15.8
isoButene Oxide	0.0	9.5	9.4
isoButyraldehyde	5.4	0.7	0.4
Carbon Monoxide	14.5	13.7	11.9
Carbon Diozide	3.1	5.2	16.9
Propylene	2.4	1.4	1.1
Methacrolein	1.5	0.8	1.0
Propylene Oxide	0.3	0.8	0.7
Acetaldehyde	0.9	0.4	0.4

In the above table, the initial production of water has been assumed equal to that of carbon monoxide.

Figure D. 31.

EFFECT OF SURFACE ON INITIAL YIELDS OF PRODUCTS.

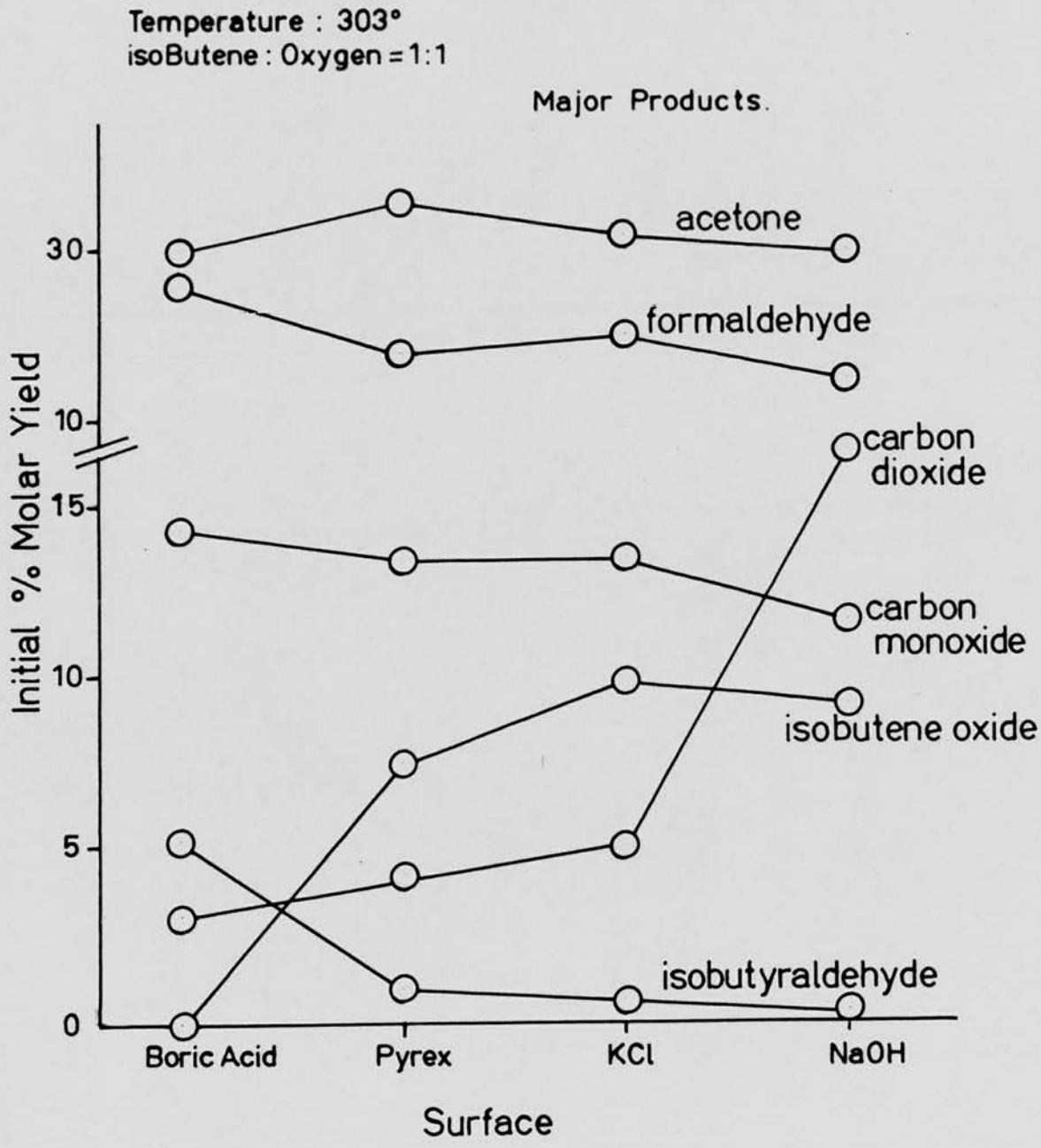
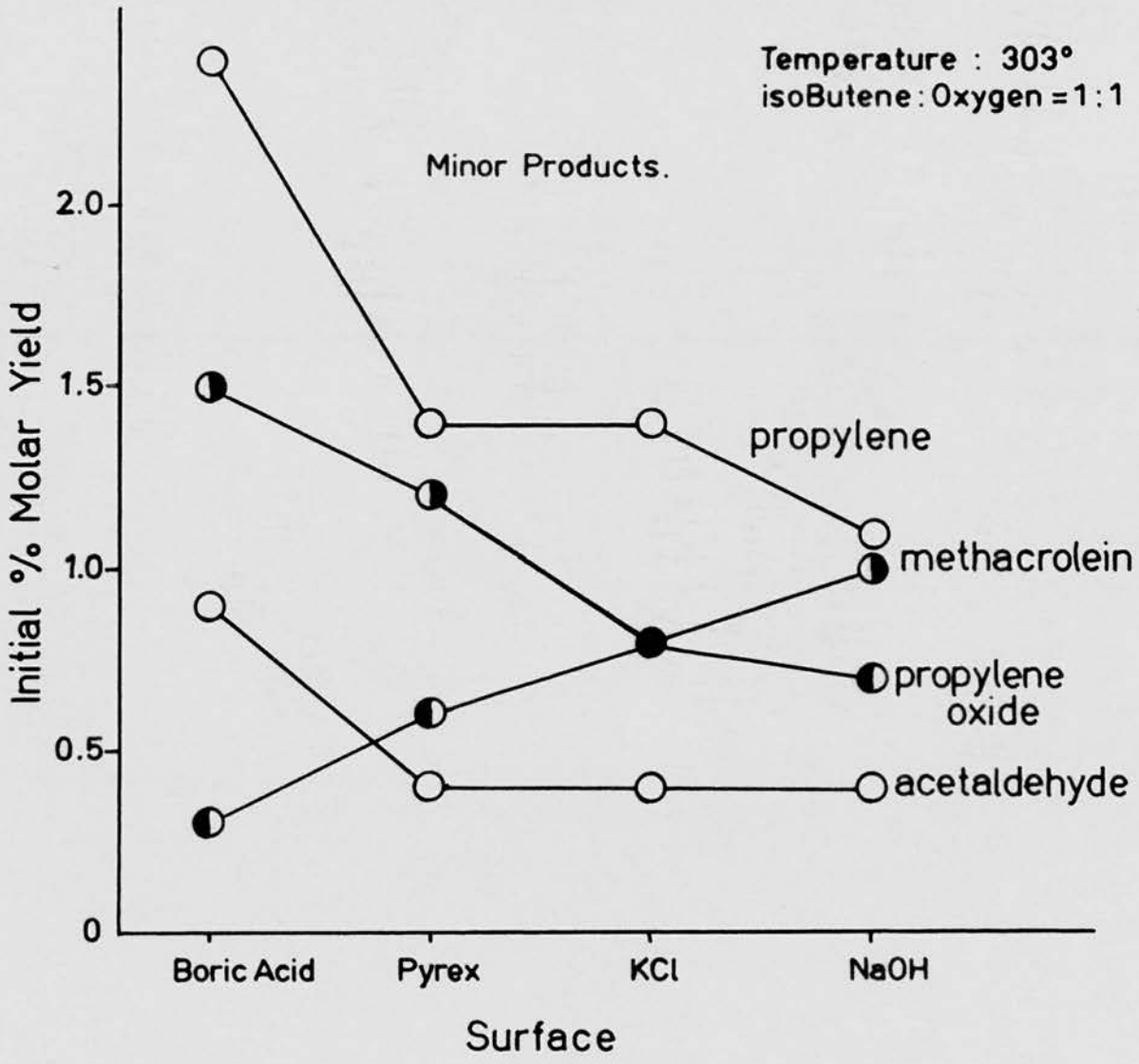


Figure D.32.

EFFECT OF SURFACE ON INITIAL YIELDS OF PRODUCTS.



3. Activation Energy Differences.

Differences in activation energy between the reaction producing acetone and those producing other products were determined according equation (1), section A. 1. 12., from which,

$$\log \text{Rate (1)}/\text{Rate (2)} = \log A_1/A_2 + (E_2-E_1)/\ 4.57T.$$

where (1) represents the reaction producing acetone,

and (2) that producing any other product X.

The rates of production of products were taken from initial gradients obtained in the last section (Figures D. 7 - D. 14.) and are given in Table D. 4. Plots of log $(Me_2CO)i/Xi$ against $1/T$ are shown in Figure D. 33. For this purpose the initial yields of isobutene oxide and isobutyraldehyde have been taken together.

The activation energy differences were obtained from the slope, (= E/4. 57), and the A factor ratios from the intercept on the 'y' axis at $1/T=0$.

The lines were not continuous over the whole temperature range, but in every case $E_2 > E_1$.

(1)	(2)		$(E_2 - E_1)$ K. Cal.	$\log A_2/A_1$
Acetone	Acetaldehyde (above 566°K0		15.5	3.7
	Propylene		16.2	4.7
	isoButene oxide	(below 576°K)	1.7	0.1
	+isobutyraldehyde	(above 576°K)	5.7	1.6
	Propylene oxide		2.7	-0.7
	Methacrolein	(below 595°K)	1.8	-0.7
		(above 595°K)	11.0	2.7

TABLE No.D.4. (fig.D.33.)

Measurement of relative activation energies.

Ratio $iC_4H_8 : O_2 = 1 : 1$

Temperature °C 1 / T°A. x 10^3	246 1.927	273 1.832	283 1.799	293 1.767	303 1.736	322 1.681	337 1.639	352 1.600
Me_2CO	0.720	0.700	0.700	0.666	0.650	0.630	0.600	0.588
iC_4H_8O	0.210	0.200	0.204	0.203	0.201	0.220	0.241	0.247
$\log Me_2CO/iC_4H_8O$	0.535	0.544	0.535	0.522	0.512	0.453	0.387	0.343
C_3H_6	0.005	0.010	0.015	0.025	0.025	0.035	0.047	0.040
$\log Me_2CO/C_3H_6$	2.158	1.845	1.669	1.426	1.415	1.255	1.106	1.167
Methacrolein	0.025	0.027	0.027	0.027	0.029	0.028	0.033	0.040
$\log Me_2CO/MA$	1.459	1.414	1.414	1.392	1.371	1.352	1.260	1.167
CH_3CHO	0.003	0.003	0.003	0.003	0.004	0.005	0.008	0.010
$\log Me_2CO/CH_3CHO$	2.380	2.368	2.368	2.346	2.211	2.100	1.875	1.769
C_3H_6O	0.007	0.010	0.012	0.012	0.011	0.012	0.012	0.012
$\log Me_2CO/C_3H_6O$	2.012	1.845	1.766	1.744	1.772	1.720	1.699	1.690

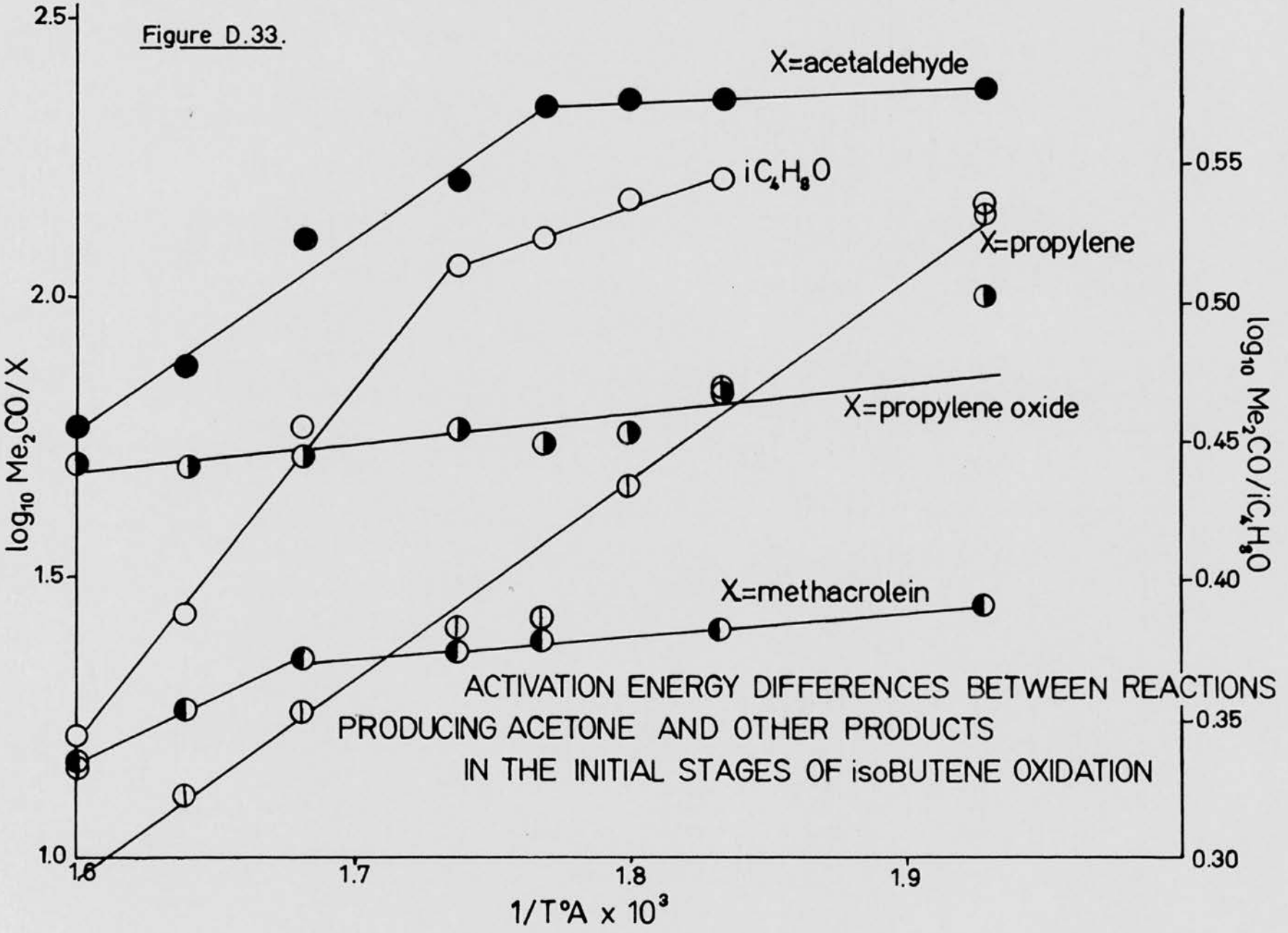


Figure D.33.
X=acetaldehyde
iC_4H_8O
X=propylene
X=propylene oxide
X=methacrolein
ACTIVATION ENERGY DIFFERENCES BETWEEN REACTIONS
PRODUCING ACETONE AND OTHER PRODUCTS
IN THE INITIAL STAGES OF isoBUTENE OXIDATION
$\log_{10} Me_2CO/X$
$\log_{10} Me_2CO/iC_4H_8O$
2.5
2.0
1.5
1.0
0.55
0.50
0.45
0.40
0.35
0.30
1.6
1.7
1.8
1.9
$1/T°A \times 10^3$

SECTION E

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

1.1 The Initiation Reaction

The exact nature of the initiation process in hydrocarbon oxidations is not known. Since slow combustions are normally carried out at temperatures between 250° and 400°, i.e. below those at which pyrolysis of hydrocarbons occurs,[123] the initiation process must involve only fuel and oxygen molecules and may well be a completely heterogeneous process. The lengths of induction periods and the magnitudes of the initial reaction rates are strongly dependent upon the nature of the reaction vessel surface indicating that the initiation process is at least in part heterogeneous.

With olefins as fuel, the reaction must involve either abstraction of a hydrogen atom or addition of oxygen to the double bond, the two simplest possibilities being those represented by reactions (1) and (2).

$$CH_2{:}C.(CH_3)_2 + O_2 \longrightarrow CH_2 - C\begin{matrix}\diagup CH_2 \\ \diagdown CH_3\end{matrix} + HO_2 \quad \ldots (1)$$

$$(CH_3)_2 . C{:}CH_2 + O_2 \longrightarrow (CH_3)_2 . \underset{O}{C} - \underset{O}{CH_2} \longrightarrow (CH_3)_2 . CO + CH_2O \quad \ldots (2)$$

Szwarc[123c] has determined the strength of the primary C - H bonds in isobutene to be about 76 k.cal. while D [H - OO] was found by Foner and Hudson[124] to be approximately 46 k.cal. Reaction (1) will, therefore, be endothermic to the extent of 30 k.cal. The activation energy for the process cannot be less than this, a value too high to suggest a homogeneous process. The activation

energy may be effectively reduced, however, if the process occurred heterogeneously on the wall of the reaction vessel.

Evidence that such an initiation process may occur has been given by Salooja[125] who found that, just as the reaction rate became measurable in the oxidation of n-heptane, the temperature at the centre of the reaction vessel was about 5° lower than in the rest of the vessel indicating a) that an endothermic reaction was occurring and, b) that in all probability it was taking place heterogeneously on the thermocouple pocket.

A similar reaction was postulated by McDowell and Thomas[126] who found that the kinetics of the oxidation of acetaldehyde could be best explained if a bimolecular reaction between acetaldehyde and oxygen was assumed to be the initiation process. Hydrogen abstraction by molecular oxygen was also proposed as the initiation step in the oxygen induced decomposition of n-butane.[127]

Reaction (2) produces an aldehyde which may itself be susceptible to oxidation and provide a source of free radicals, possibly at the walls of the reaction vessel (see Section A.1.8).

The alternative addition of oxygen to the double bond to give a diradical has been postulated by Bolland and Gee[128] as a probable process in liquid phase oxidations:

$$R.CH:CH.CH_2.R' + O_2 \longrightarrow R.\underset{\underset{OO}{|}}{CH}.CH.CH_2.R'$$

They calculated that the reaction would be endothermic by about 14 k.cal.. The formation of peroxy diradicals of this type has not gained much support as

a very probable reaction in gas phase systems.

Oxidations 1 - 9, (Figures C.1 - C.9) show that below 300° the reaction products are produced initially at a maximum rate. Propagation steps in the oxidation will lead if anything to an overall decrease in the radical concentration due to wall destruction of hydroperoxy radicals. Since the rate of production of oxidation products decreases with time, branching reactions, which are normally the greatest source of fresh radicals once the reaction gets under way, cannot be important below 300°. The initiation process therefore becomes the main source of radicals starting fresh chains below this temperature.

Although no direct evidence is available as to what the initiation reaction might be, the production of hydroperoxy radicals is indicated by the fact that the reaction proceeds much faster in a boric acid coated vessel, which is known to preserve hydroperoxy,[129] than in a clean pyrex vessel.

1.2 The early stages of the oxidation

Acetone and formaldehyde were the major products formed in the early stages of the oxidation between 246° and 352°. A variety of minor products were also produced early in the reaction. Initial product analysis, in some cases below an isobutene conversion of 1%, showed that below 300° initial products besides acetone and formaldehyde were isobutene oxide, acetaldehyde, propylene oxide, methacrolein, propylene, carbon monoxide and water. Above 300°, isobutyraldehyde and carbon dioxide were also initial products.

The ratio of acetone to formaldehyde varied from 2 : 1 to almost 3 : 2 under different reaction conditions, the difference between the two being made up by the yield of carbon monoxide. Although the pressure time curves showed an initial pressure decrease and an overall sigmoid shape (Figure C.31.) product development with time was not autocatalytic below about 310°, the production of major and minor products starting at their maximum rate below this temperature. The distribution of products stayed constant for 15-50% of reaction indicating that up to this stage isobutene was the most reactive species in the system.

The molar distribution of products in the early stages of reaction, calculated from measurements of the initial gradients, is given in Tables D.1 - D.2.

The formation of equivalent quantities of formaldehyde and acetone in the same reaction was postulated by Skirrow and Williams[94] to be produced by the process given on page 49, but an equally plausible scheme involving an HO_2

radical chain would be:

$$(CH_3)_2.C:CH_2 + HO_2 \longrightarrow (CH_3)_2.C-CH_2OOH \quad \ldots\ldots \quad (3)$$

$$\text{or} \quad (CH_3)_2.\underset{\displaystyle OOH}{\overset{\displaystyle |}{C}}-CH_2 \quad \ldots\ldots \quad (3a)$$

$$(CH_3)_2.C-CH_2OOH \longrightarrow (CH_3)_2.C.OH + CH_2O \quad \ldots\ldots \quad (4)$$

or

$$(CH_3)_2.\underset{\displaystyle OOH}{\overset{\displaystyle |}{C}}-CH_2 \longrightarrow (CH_3)_2.CO + CH_2OH \quad \ldots\ldots \quad (4a)$$

followed by the oxidation of the resulting radicals

$$CH_2OH + O_2 \longrightarrow CH_2O + HO_2 \quad \ldots\ldots \quad (5)$$

$$(CH_3)_2C.OH + O_2 \longrightarrow (CH_3)_2.CO + HO_2 \quad \ldots\ldots \quad (5a)$$

This scheme involves only attack at the double bond. Evidence that radical attack on olefins occurs mainly by addition to the double bond has been given by the results of many workers from studies of systems involving olefins and small alkyl radicals and hydrogen atoms. For example, the activation energy for the addition of methyl and ethyl radicals to various olefins[130] have been found to be consistently of the order 6-8 k.cal.mole^{-1}, while the activation energy for the addition of hydrogen atoms[131] is probably as low as 2k.cal.mole^{-1}. On the other hand, the activation energy for hydrogen abstraction by the same radicals[132] has been determined to be normally of the order of 10k.cal.mole^{-1}.

Szwarc[133] determined that the ratio of addition/abstraction occurring in the reaction of methyl radicals with isobutene in iso-octane solution was about 16 : 1 at 65°.

Rust, Seubold and Vaughan[134] found that methyl radicals added to both terminal and non terminal carbon atoms at 253° in a flow system. The abstraction reactions of methyl, ethyl and hydrogen are all much more exothermic than hydroperoxy, so if this species is in fact the principle fuel attacking radical the evidence is strongly in favour of reaction (3) occurring.

Walsh[109] postulated that the most likely bonds to break during the decomposition of peroxides or peroxy radicals would be the 0 - 0 linkage and the adjacent C - C linkage e.g. di-t-butyl peroxide decomposes[135]

$$(CH_3)_3.C\text{-}0\text{-}0\text{-}C.(CH_3)_3 \longrightarrow 2(CH_3)_3.C0$$

$$(CH_3)_3.C0 \longrightarrow CH_3 + (CH_3)_2.C0$$

In the case of reaction (4) an analogous scission to this would give

$$(CH_3)_2.C\text{-}CH_2\,00H \longrightarrow (CH_3)_2.C + CH_20 + 0H$$

This would lead to a highly branched reaction which was not in agreement with the experimental results. The fate of the diradical produced would most likely be rearrangement to propylene which although an initial product at all times was not a major product. The formation of acetone and formaldehyde as the major products makes the only acceptable decomposition of $C_4H_8$00H :

$$(CH_3)_2.C(OOH) - CH_2 \longrightarrow \left[(CH_3)_2.C - CH_2 \;\; O\cdots O\text{-}H\right] \longrightarrow (CH_3)_2.CO + CH_2OH$$

similarly for the alternative radical $(CH_3)_2.C.CH_2OOH$

The evidence for reactions (5) and (5a) is very strong. Bell and Tipper[86] postulated that this reaction occurs in the oxidation of methyl alcohol. The intermediate peroxy radical will have to isomerise before the products are produced:

$$CH_2OH + O_2 \rightarrow HO.CH_2OO \rightarrow O.CH_2OOH \rightarrow CH_2O + HO_2 \qquad \ldots\ldots (6)$$

Semenov[136] has estimated that the activation energy for reaction (7), which is thought to occur in the oxidation of methane, is about 20 k.cal.mole^{-1}.

$$CH_3OO \longrightarrow CH_2OOH \qquad \ldots\ldots (7)$$

With $HO.CH_2OO$, however, the O-H bond is very much weaker than the C-H bond in methyl peroxy and the isomerisation in reaction (6) will have a much lower activation energy. The decomposition can then proceed only by one of the following reactions :

$$O.CH_2.OOH \longrightarrow CH_2O + HO_2 \qquad \ldots\ldots (8)$$

$$O.CH_2.OOH \longrightarrow CH_2O_2 + OH \qquad \ldots\ldots (9)$$

In order to satisfy the experimental results the product of the reaction must be formaldehyde and since the only possible product of the formula CH_2O_2 would be formic acid, and this only after a very drastic rearrangement of $O.CH_2.O$,

the only acceptable reaction is (8).

The same argument holds for the $(CH_3)_2.C.OH$ radical.

A feature of the present work was the low ratio of formaldehyde to acetone. This was similar to the results of Mullen and Skirrow[108] and of Skirrow[65] in the oxidations of propylene and hex-1-ene, where the ratio of formaldehyde to other aldehydes was low, but in contrast to those of Skirrow and Williams, (see above), who obtained a molar ratio of formaldehyde to acetone of 1 : 1.

It is difficult to account for a ratio of less than 1 : 1 by the mechanism of Skirrow and of Cullis, (see [93]), whereas by the hydroperoxy chain reaction (5) may be re-placed to some extent by reaction (10).

$$CH_2OH + O_2 \longrightarrow CO + H_2O + OH \quad \ldots\ldots\ldots (10)$$

The ensuing hydroxyl radicals would then probably be converted to hydroperoxy by the following route :

$$XH + OH \longrightarrow X. + H_2O$$

$$X + O_2 \longrightarrow Y + HO_2$$

where X. is a radical which produces Y on removal of a hydrogen atom

That the acetone yield was always greater than that of formaldehyde is evidence that an analogous degradation of the hydroxy isopropylidene radical does not occur to any appreciable extent.

The major initial reaction can therefore be represented:

$$C_4H_8 + (1+x)O_2 \longrightarrow (CH_3)_2.CO + (1-2x)CH_2O + 2\,x\,CO + 2\,xH_2O$$

1.3 Dependence on reactant pressure

The dependence of product distribution on initial oxygen pressure was studied in Oxidations 1-3 (Figures C.1.-C.3.)

Of the products examined by gas chromatography, (excluding formaldehyde), the initial yield of acetone, over the four fold variation in oxygen pressure, increased by only 4%, isobutene oxide yield decreased by 7%, while that of propylene decreased by 60%. Over the isobutene to oxygen pressure range 100:100; 100:200, the initial yields of methacrolein and propylene oxide both decreased by 50 % while that of acetaldehyde increased by 65%.

Although the initial yields of acetone and isobutene oxide were virtually independent of oxygen pressure, the reason for such a wide distribution in the initial yields of the other products was not obvious, unless the radical (A), produced by addition of hydroperoxy to the double bond, underwent further oxidation to the peroxy radical (B), giving rise to a scheme similar to that proposed by Knox and Wells[82]:

$$C_4H_8OOH \underset{(A)}{} + O_2 \longrightarrow OO.C_4H_8.OOH \underset{(B)}{} \longrightarrow Me_2CO + CH_2O + HO_2$$

(A) $\downarrow$ Q

(B) $\downarrow O_2$ P

The yields of the products P and Q would then be dependent upon oxygen pressure, while the yield of acetone would be relatively unaffected. Products corresponding to P would obey the kinetic law:

$$[P] \; / \; [\text{Acetone}] = k_1 [O_2]$$

whereas products corresponding to Q would follow the relationship:

$$[Q] / [\text{Acetone}] = k_2 / [O_2]$$

isoButene pressure, varied over the same range (Oxidations 1, 4 and 5), caused a 12% decrease in the initial yield of acetone, accompanied by an increase in the yields of isobutene oxide and propylene of 37% and 25% and of methacrolein and propylene oxide over the pressure range isobutene: oxygen 100:100; 200:100, of 50% and 30% respectively. The initial yield of acetaldehyde decreased by 50%

Large fluctuations in intial yields of minor products as indicated above are difficult to account for by any of the homogeneous processes already described. The relative constancy of the acetone yield with respect to oxygen and isobutene pressure variations indicates that the reaction proposed for its production conforms to the accepted homogeneous reaction schemes but the wide variation of the minor product yields cannot be simply explained.

1.4. Effect of temperature.

The effect of raising the temperature stepwise over the range 246° -352°,(Oxidations 1-13), was to increase the yields of minor products at the expense of those of acetone, formaldehyde and isobutene oxide.

The initial yield of acetone fell gradually over the range, the initial production at 352° being 18% less than at 246°. A feature of increasing the temperature was the appearance of isobutyraldehyde in the products at 293° and its continued increase with increasing temperature until it accounted for 14% of the total carbon in the products at 352°. The initial yield of isobutene oxide decreased by 43% over the range while the yields of all the other products except propylene oxide increased with increasing temperature. The initial yield of propylene oxide, except for the run at 246°, remained steady over the whole temperature range.

The yield of carbon monoxide increased by a factor of 2.3, while that of carbon dioxide rose from zero at 246° to account for 4% of the total carbon in the products at 352°. Of the remaining products the initial yields of methacrolein and acetaldehyde increased by 60% and 23% respectively, while that of propylene increased by a factor of four.

Activation energy differences.

One of the original aims of the research was to measure the differences in activation energy between reactions producing primary products of the oxidation by the method outlined earlier, (page 56). From present oxidation theories, whereby all the products of the reaction are considered

as arising from the homogeneous decomposition of one or two similar radicals, one would not expect a difference of more than a few k. cal. mole^{-1} between the activation energies of the competing reactions.

Figure D. 33. shows plots of log of the ratio of the initial yields of acetone to other reaction products, against the reciprocal of the absolute temperature. Many of the plots were not continuous straight lines over the whole temperature range, a break appearing at about 570°K.

The activation energy for the reaction producing acetone was lower than that producing any other product except isobutene oxide, the differences (see page 147) in some cases being much greater than would be expected for competing homogeneous processes. The values corresponding to the production of propylene and acetaldehyde were particularly high which is not unexpected since there is no obvious route to either of these products from isobutene, and their formation must involve the breaking of many bonds and atom rearrangements.

This, along with the evidence outlined earlier suggested that essentially homogeneous processes could not account for all the reaction products.

1.5. Effect of surface.

The wide variation in the yields of minor products in the initial stages of the reaction under different experimental conditions, coupled with the large activation energy differences between some of the reactions outlined in the previous section, suggested that the reaction vessel surface may have played a more significant role in the formation of products than had been imagined.

Surface effects were studied in Oxidations 14-22 using a range of surfaces from acidic to basic at 303°. The results obtained using coated vessels were compared with those obtained using a clean pyrex vessel. The results obtained with any particular surface altered with successive runs, especially in a boric acid coated vessel, so that three runs were carried out with each surface after the reaction vessel had been conditioned according to the procedure outlined previously. (Section B.3.2.) The difference between results obtained on any one surface was never as great as between the results from runs in the coated and uncoated vessel.

The boric acid coated vessel provided the most striking results. In the 'aged' vessel, i.e. after the third oxidation the yield of acetone was reduced only slightly compared with that in the uncoated vessel. The yield of isobutene oxide decreased with successive runs and was below the detectable limits of the analytical system during the initial stages of the third oxidation. The epoxide was replaced by a roughly equivalent amount

of isobutyraldehyde (see page 135). This surface also caused a suppression of propylene oxide while the yield of its isomer propionaldehyde was greater than under any other experimental conditions. The initial yield of acetaldehyde was increased by a factor of 1.5 compared to that on clean pyrex while the yield of methacrolein, although only slightly greater than that obtained using clean pyrex, was much greater than with any other surface. Of the carbon oxides, the initial yield of carbon monoxide increased by 12% while that of the dioxide decreased by 20% compared with their corresponding yields in a pyrex vessel.

The results obtained using this surface were similar to those obtained by Skirrow and Williams using a clean pyrex vessel in that isobutyraldehyde rather than isobutene oxide was now the third major oxygenated product.

In a potassium chloride coated reaction vessel the product distribution was similar to that obtained using clean pyrex. The yield of acetone increased by 24% over the yields in clean pyrex. The increased yield of isobutene oxide was accompanied by a corresponding decrease in that of isobutyraldehyde. The initial yields of carbon monoxide, propylene and acetaldehyde were approximately the same as in the clean pyrex vessel while those of carbon dioxide and methacrolein decreased by 36% and 17% respectively.

The initial product distribution using a sodium hydroxide coated vessel was similar to that obtained with a potassium chloride surface. The only major changes were in the yields of carbon dioxide, which increased a

by a factor of four, and isobutyraldehyde which decreased by 50% over their initial yields in the pyrex vessel. The yield of acetaldehyde was the same as that obtained using both clean pyrex and potassium chloride coated vessels, while that of methacrolein was the same as was obtained with the potassium chloride surface. Similarly, compared with the corresponding oxidations in the potassium chloride coated vessel, the initial yields of propylene and carbon dioxide decreased slightly, (12% and 8% respectively), while the yield of propylene oxide increased slightly.

The initial yield of acetone was least disturbed by variation of the surface coating but showed a gradual decrease over the range clean pyrex-boric acid-potassium chloride-sodium hydroxide. The unpredictably wide variation in the initial yields of minor products with different surface coatings added substance to the idea that the nature of the reaction vessel surface played a big part in the formation of minor products.

2. The isomerisation of isobutene oxide.

The isomerisation of isobutene oxide was studied separately to determine whether isobutyraldehyde was an alternative product to isobutene oxide or if it was produced by thermal or surface isomerisation of the epoxide. This was not obvious from the plot of isobutyraldehyde development/extent of reaction (Figure D. 12.) since, as the aldehyde was probably the species most vulnerable to further attack in the system, any upward trend in the plot from the initial formation rate due to isomerisation would be counteracted by a drop in yield due to further oxidation. Under most conditions where isobutyraldehyde was formed, the yield as the reaction progressed fell below the initial rate of production indicating that oxidation of the aldehyde predominated over isomerisation of the epoxide.

Little is known of the thermal uncatalysed isomerisation of epoxides although gas phase conversions of these to the corresponding aldehydes have been carried out catalytically in high yield. Jacobs and Lundsted,[137] using a $Cr_2O_3/CdO/CdCl_2$ catalyst in a flow system at 300°, obtained conversions of about 70% for the isomerisation of ethylene and propylene oxides to the corresponding aldehydes. The same conversion was obtained by Robeson and Springer[138] using a flow system at 315° and "Fuller's Earth" catalyst.

The isomerisation was studied first in a sodium hydroxide coated vessel which had given yields of isobutyraldehyde and isobutene oxide similar to those obtained in a clean pyrex vessel. The isomerisation fitted a first order rate law at 309° 325° and 356°, (Figure C. 37.), with rate constants

of 1.75×10^{-6}, 6.50×10^{-6} and 2.80×10^{-5} sec^{-1} respectively. Although the system was not controlled stringently enough to allow the accurate calculation of Arrhenius parameters from the data, the apparent activation energy derived from the three rate constants was 46k. cal. $mole^{-1}$ and an A factor of 10^{10} sec^{-1}. The low values obtained for the activation energy and A factor, compared to Frost and Pearson's[139] values of 58k. cal. $mole^{-1}$ and 10^{14} sec^{-1} for the unimolecular gaseous decomposition of propylene oxide, suggest that in the present system the isomerisation was at least partly surface catalysed.

Subsequent oxidation experiments in the same vessel at 309° and 359° on isobutene/oxygen mixtures containing some isobutene oxide, showed that at 309° the rate of production of isobutyraldehyde at an early stage of the reaction was about 10^{-3} mm. Hg. $sec.^{-1}$ and up to almost 50% conversion of isobutene did not fall below 2×10^{-4} mm. Hg. $sec.^{-1}$, whereas the isomerisation rate of the isobutene oxide present would be 1.6×10^{-5} mm. Hg. $sec.^{-1}$ At 359° the rate of production of isobutyraldehyde was 1.5×10^{-3} mm. Hg. $sec.^{-1}$ corresponding to an isomerisation rate of 2×10^{-4} mm. Hg. $sec.^{-1}$ The results indicated that isobutyraldehyde was being produced at least five times faster than it would have been solely by isomerisation.

In a boric acid coated reaction vessel the isomerisation of the oxide occurred at a very fast rate, about 90% of the initial oxide being converted to isobutyraldehyde in one minute, irrespective of the initial pressure. Similarly, in an oxidation run on a mixture containing isobutene oxide, almost

all the oxide present at the start was converted to aldehyde inside the first minute of reaction.

The experiments showed that in the sodium hydroxide coated vessel the isomerisation although probably a surface process could not account for all the isobutyraldehyde produced and the same probably holds for a clean pyrex vessel as well. No attempt was made to recreate a clean pyrex surface since the reaction vessel had already undergone many surface treatments and a surface of the same activity as the original could not be guaranteed. In a boric acid coated vessel, it would appear that isobutene oxide would be rapidly converted to isobutyraldehyde and that in Oxidation Nos. 14-16, the precursor to isobutyraldehyde was almost certainly isobutene oxide.

3.1. Later stages in the oxidation.

After the initial rapid reaction the oxidation system contains a mixture of products some of which are themselves susceptible to oxidation for example formaldehyde, methacrolein, propylene and isobutyraldehyde (above 300°). The increased rate of production of degradation products, carbon monoxide, carbon dioxide, and water as the reaction proceeds indicates that further oxidation occurs to some extent. Up to about 20-30% of the isobutene consumption the distribution of products remains virtually constant, showing that isobutene up to this stage is the substance undergoing the greatest attack. With the decline in isobutene concentration, however, the rate of isobutyraldehyde production falls rapidly to zero, despite the fact that isomerisation of isobutene oxide will tend to increase its concentration. The oxidation of acetaldehyde and higher aldehydes up to 200° is believed to proceed by the following general series of reactions:[140]

$$R.CHO + O_2 \longrightarrow R.CO + HO_2 \quad \ldots\ldots\ldots(1)$$

$$R.CO + O_2 \longrightarrow R.CO_3 \quad \ldots\ldots\ldots(2)$$

$$R.CO_3 + RH \longrightarrow RCO_3H + R \quad \ldots\ldots\ldots(3)$$

$$R.CO_3H \longrightarrow R + CO_2 + OH \quad \ldots\ldots\ldots(4)$$

At temperatures above 250° reaction (2) will be replaced to a large extent by reaction (5).

$$R.CO \longrightarrow R + CO \quad \ldots\ldots\ldots(5)$$

The fate of the alkyl radical R will be dependent upon reaction conditions. As the oxygen content in the reaction vessel decreases and there exists an

increasing number of products with weak C-H bonds, the relative importance of hydrogen abstraction compared to oxidation will become more pronounced.

Above 300° isobutyraldehyde appears to be the most susceptible of the products to attack. Since the stability of carbonyl radicals decreases with increasing chain length,[141] oxidation of isobutyraldehyde may be represented by reactions (6) and (7).

$$(CH_3)_2.CH.CHO + O_2(HO_2) \longrightarrow (CH_3)_2.CH.CO + HO_2\ (H_2O_2) \quad \ldots\ldots(6)$$

$$(CH_3)_2.CH.CO \longrightarrow (CH_3)_2.CH + CO \quad \ldots\ldots\ldots(7)$$

When sufficient oxygen is available the fate of the isopropyl radical will be oxidation to propylene according to reaction (8)

$$(CH_3)_2.CH + O_2 \longrightarrow CH_3.CH{:}CH_2 + HO_2 \quad \ldots\ldots\ldots(8)$$

The absence of propane and ethylene in the reaction products, even when the oxygen concentration was low, suggested that reaction (7) was throughout followed by reaction (8). Also, the yield of propylene increased above its initial rate of production as that of isobutyraldehyde decreased. For example, in the runs in the boric acid coated vessel where isobutyraldehyde production was particularly high, propylene production increased substantially above its initial production rate, whereas in the potassium chloride coated vessel, where the aldehyde was largely replaced by isobutene oxide, the yield of propylene fell below its initial production rate at intermediate stages of the oxidation.

That methacrolein did not vary much from its initial rate of formation suggests that it was not attacked to any serious extent.

The appearance of methyl alcohol in hydrocarbon oxidation systems has proved difficult to explain satisfactorily. In the present system it appeared in the reaction products in small quantities when the oxygen was nearly exhausted.

An obvious precursor to methanol is methoxy, producing the alcohol by hydrogen abstraction:

$$CH_3O + RH \longrightarrow CH_3OH + R \quad \ldots\ldots\ldots (9)$$

but Hanst and Calvert[142] have shown that methoxy is readily oxidised to formaldehyde at temperatures as low as 150°, by reaction (10):

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \quad \ldots\ldots\ldots (10)$$

which is exothermic to the extent of 20k. cal.

This suggests that methoxy will normally undergo oxidation (see page 52) to formaldehyde but, at later stages in the reaction when oxygen is rarer and relatively more weak C-H bonds are available, methanol will result by reaction (9). The hydrogen donor may be formaldehyde itself since Subbaratnam and Calvert[143] showed that reaction (11) can occur at temperatures as low as 20°.

$$CH_3O + CH_2O \longrightarrow CH_3OH + CHO \quad \ldots\ldots\ldots (11)$$

In systems where acetaldehyde is a major product[41, 93, 144] large quantities of methanol are produced. Neiman, Efremov and Serdyuk[144] have shown that, in the oxidation of propylene, most of the methanol produced came from acetaldehyde via the acetyl peroxy radical but that some came from methyl radicals. The latter route was suggested by

Fisher and Tipper[145], the methanol supposedly arising from the heterogeneous decomposition of intermediate methyl hydroperoxide.

Although acetaldehyde was a minor product of the present oxidation, it may have contributed to the small amounts of methanol produced.

If, however, hydroxy methylene is formed in the propagation steps of the oxidation as suggested, hydrogen abstraction by this radical seems a more likely source of methanol, although abstraction by this radical is much less exothermic than by methoxy:

$$CH_2OH + CH_2O \longrightarrow CH_3OH + CHO \qquad H = +2 \text{ k.cal.}$$

or $$CH_2OH + (CH_3)_2.C{:}CH_2 \rightarrow CH_3OH + CH_2{:}C(CH_3).CH_2 \qquad H = -8 \text{k. cal.}$$

this again is in keeping with the fact that methanol appears only when the oxygen concentration is low.

The presence of small quantities of methane towards the end of the oxidation can only be explained by hydrogen abstraction by methyl radicals. Although acetaldehyde cannot be confirmed as the molecular precursor of methanol, the oxidation of this aldehyde seems the only obvious molecular source of methyl radicals. Indirect evidence of this was given in the reactions in the boric acid coated vessel where the increased yield of acetaldehyde was reflected in the increased yield of methane later in the reaction, so that the route to methane in the absence of large quantities of oxygen may be:

$$CH_3CHO + O_2 \longrightarrow \underset{+\ HO_2}{CH_3CO} \longrightarrow \underset{+\ CO}{CH_3} \xrightarrow{XH} CH_4 + X$$

In the presence of excess oxygen the fate of the methyl radical would most likely be oxidation to formaldehyde:

$$CH_3 + O_2 \longrightarrow CH_2O + OH$$

This reaction has been accepted as a chain propagating step in the oxidation of methane[146] and has been confirmed by McKellar and Norrish[147] who observed the spectra of hydroxyl and formaldehyde in the flash photolysis oxidation of methyl iodide.

The likeliest source of the trace quantities of propionaldehyde which occurred late in the reaction and to a greater extent in the boric acid coated vessel would be radical attack on propylene, similar to the mode of formation of isobutyraldehyde from isobutene. Another possible source would be by isomerisation of propylene oxide the yield of which showed a marked decrease in the oxidations in the boric acid coated vessel.

There is no evidence from the shape of the product development/extent of reaction curves (Figure D. 8.) that formaldehyde suffered oxidation to a great extent in the regions in which it was analysed although it may have acted as a hydrogen donor at later stages in the reaction. This is in accordance with reaction (11) where although the activation energy is not known it is not expected to be high and the formyl radical has been shown by Malmberg[148] to have an appreciable lifetime at temperatures greater than 500° so that reaction (12) may not occur extensively at the temperatures of the present oxidations although such a reaction would be very exothermic:

$$HCO + O_2 \longrightarrow HO_2 + CO \qquad \ldots\ldots\ldots(12)$$

Similarly, the analytical results for the formation of propylene gave little indication that it was participating in further reactions.

3.2 Degradation Products

The formation of carbon monoxide and water as alternatives to formaldehyde in the major oxidation process has already been indicated. Parallel formation of the two occurred throughout the reaction. The mode of formation of the two products is not known but the formation of carbon monoxide and water by action of oxygen on hydroxymethylene would require the formation and breaking of too many bonds for it to be a likely homogeneous process and a more likely route would be:

$$CH_2OH + O_2 \rightarrow \left[OO-\overset{H}{\underset{H}{C}}-OH \right] \xrightarrow{\text{wall}} CO + H_2O + OH \quad \ldots (13)$$

The formation of carbon dioxide, especially early in the reaction, suggests than an alternative route for the intermediate formed in (13) would be:

$$\left[OO-\overset{H}{\underset{H}{C}}-OH \right] + O_2 \xrightarrow{\text{wall}} CO_2 + H_2O + HO_2 \quad \ldots (14)$$

At 273° the initial yields of carbon dioxide were small, but in reactions containing excess oxygen the initial ratio of $CO:CO_2$ was decreased indicating that the two competing reaction (13) and (14) may occur.

As the temperature was increased the ratio of $CO:CO_2$ would have been expected to increase also since any aldehyde degradation would be expected to occur at elevated temperatures by reaction (15)

$$R.CHO + O_2 \longrightarrow \begin{matrix} RCO \\ + \\ HO_2 \end{matrix} \longrightarrow R + CO \quad \ldots (15)$$

The ratio of the yields of $CO:CO_2$ did in fact decrease slightly above 300° and

carbon dioxide definitely became an initial product. The decrease in the ratio my be due to reaction (14) becoming more important as the temperature is raised, i.e., the activation energy of (14) my be greater than that of (13) or carbon dioxide is being produced by another route at higher temperatures.

The initial yield of the dioxide in a sodium hydroxide coated vessel increased by a factor of six over its initial rate of production in a clean pyrex vessel, clearly indicating that its formation was by a heterogeneous process. This was confirmed by Knox and Turner[149]. in the oxidation of isobutane in a silver plated vessel where the initial yield of carbon dioxide accounted for 70% of the isobutane consumed in early stages.

3.3. Termination reactions.

The ultimate fate of hydroperoxy radicals during oxidation reactions depends on how they react with the reaction vessel walls. The elucidation of chain termination reactions by heterogeneous radical destruction has been mainly due to Walsh. Hoare and Walsh[150] found that in the slow combustion of methane at 500° autocatalysis was eliminated by coating the reaction vessel with lead oxide. Chamberlain, Hoare and Walsh[151] argued that HO_2 was the most likely species to be formed by the degenerately branching reaction in the oxidation, since, with the possible exception of HCO_3 radicals all the other likely chain carriers would be so reactive that they would react before reaching the wall. If, for example, OH had been produced by the branching reaction, autocatalysis should have ensued no matter the nature of the surface.

The effect of varying the reaction vessel coating on the kinetics of the methane oxidation, led Walsh et al. to classify surface coatings in three groups:

Group A: Surfaces which preserve HO_2 (and H_2O_2). Surface coatings in this group are acidic in nature e.g., boric acid, silicic acid etc., which are believed to initially donate a proton to the absorbed species. After a further reaction cycle hydrogen peroxide is produced and the proton regenerated:

$$HO_2 + \left[H^{+}\right] \longrightarrow \tfrac{1}{2}H_2O_2 + \tfrac{1}{2}O_2 + \left[H^{+}\right]$$

The hydrogen peroxide can then enter the reaction by homogeneous fission to hydroxyl radicals, if the temperature is high enough, which will initiate fresh chains.

Group B: Surfaces comprised of strong electron donors such as noble metals which are known to destroy peroxides rapidly.

Group C: This group is made up of weaker electron donors e.g., metal oxides, salts and bases, whose peroxide destroying properties fall between those of Groups A and B.

$$HO_2 + [\epsilon] \rightarrow\rightarrow \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2 + [\epsilon]$$

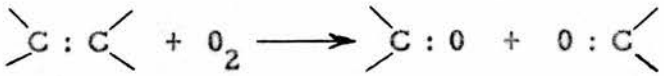
The chain termination step in the region of the second explosion limit in the hydrogen/oxygen reaction has been accepted as due to heterogeneous destruction of hydroperoxy. The effect of using reaction vessels with surface coatings of Groups A, B and C substantiated this view. Warren[152], however, showed by separate studies using oxygen and hydrogen atoms that, although surface coatings fell into three groups as proposed by Walsh, surfaces in any particular category were unselective in the radicals they preserved or destroyed so this method could not be used to differentiate between radical species.

In the isobuteme oxidation the reaction in a boric acid coated vessel proceeded much faster than in a clean pyrex vessel. On the other hand, the rate of reaction in potassium chloride and sodium hydroxide coated vessels were about the same and little slower than that in the clean pyrex vessel. This suggested that the original pyrex vessel surface was more basic than acidic in nature.

4. Kinetics of the reaction

4.1 Initial pressure decrease

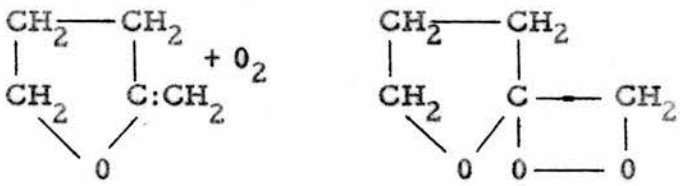
The most striking kinetic feature of olefin oxidations is the initial pressure decrease which precedes the period of rapid pressure increase and which is normally of the order of 1-2% of the olefin pressure. Since cleavage of the olefinic bond to yield equivalent amounts of two carbonyl compounds according to the stoichiometric equation:



produces no overall pressure change, the pressure decrease must be attributable to a minor process. There have been various tentative explanations of the pressure decrease, none of which has been substantiated by convincing experimental proof.

a) Formation of ring peroxides

The formation of cyclic peroxides by the addition of an oxygen molecule across a double bond was first suggested by Ubbelhode[34] in 1935 as a step in the peroxidation of unsaturated ring compounds.



Later, Dobrinskaya and Neiman[118] suggested a four membered ring peroxide as a primary intermediate in the oxidation of but-2-ene.

Cullis, Fish and Turner[93] postulated the same reaction as a

frequent initiation step in the oxidation of 2-methyl but-2-ene.

$$(CH_3)_2.C{:}CH.CH_3 + O_2 \longrightarrow (CH_3)_2.\underset{O}{C} - \underset{O}{CH}.CH_3$$

Such a reaction, besides leading to a pressure decrease could also explain the formation of equivalent quantities of the two major carbonyl compounds, (the latter has already been discussed). The quantities of peroxide obtained in the oxidation could in fact be correlated to the extent of pressure decrease and the isolation of small quantities of 2-methyl 2, 3-dihydroxy butane obtained on treating the reaction products with lithium aluminium hydride suggested that this reaction may occur to some extent.

b) Polymerisation

The discovery by Burgoyne and Cox[153] that hydrocarbons with more than three carbon atoms were formed in the oxidation of ethylene at 515° provided evidence that radical polymerisation could occur in oxidation systems. Polymerisation was suggested by Blundell and Skirrow[91] and Skirrow[65] to account for the pressure decrease observed in the oxidations of hex-1-ene and but-2-ene between 290° and 395° and was assumed to account for the loss of carbon and hydrogen in the oxidation of isobutene by Skirrow and Williams[94]. However, since these workers did not analyse for higher hydrocarbons it was not possible to decide whether or not radical polymerisation occurred.

Cullis (see sub-section a) suggested polymerisation as an alternative to ring peroxide formation by an analogous reaction to that occurring

in liquid phase oxidation systems involving copolymerisation of the olefin and oxygen, followed by the breakdown of the polymer:

$$(CH_3)_2.C{:}CH.CH_3 + RO_2 \rightarrow (CH_3)_2.C(-O-O-R)-CH.CH_3$$

followed by the further alternative addition of olefin and oxygen leading to chains such as:

$$(CH_3)_2.C(-O-O-)-CH.CH_3 \quad (CH_3)_2.C(-O-O-)-CH.CH_3 \quad (CH_3)_2.C(-O-O-)-CH.CH_3 \quad (-O-O-R)$$

Besides accounting for the initial pressure decrease this scheme also accounted for the products of the oxidation by fission of the appropriate C-C and 0-0 bonds[109].

This explanation was not completely satisfactory since under oxygen deficient conditions polymers would result of the type:

$$(CH_3)_2.C(-O-O-)-CH.CH_3 \quad (CH_3)_2.C(-O-O-)-CH.CH_3 \quad CH_3.CH-C.(CH_3)_2 \quad (CH_3)_2.C(-O-O-)-CH.CH_3$$

which on decomposition would yield hydrocarbon products of the type $CH_3.CH{:}CH.CH_3$ and $(CH_3)_2.C{:}C.(CH_3)_2$, which were not observed experimentally.

c) Hydroperoxide formation

One of the advantages of the peroxide theory of degenerate branching (page 20) was that initial formation of hydroperoxides represented by the stoichiometric equation:

4.2 dP/dt as a measure of reaction rate

In alkane oxidations it has been established that the proportionality factor between the rate of pressure change, (dP/dt), and the rate of reaction measured by the rate of consumption of oxygen or hydrocarbon, or rate of formation of products, is a constant. The rate of pressure change can therefore be used as a measure of the reaction rate.

Except in the oxidation of propylene by Mullen and Skirrow,[108] who showed that the proportionality factor between the maximum rate of pressure change and maximum rate of oxygen consumption was a constant, pressure changes have never been used to measure the reaction rate in olefin oxidations.

In the isobutene system the relationship between dP/dt, dO_2/dt, dMe_2CO/dt was investigated. A plot of the development of the three against time in Oxidations Nos. 10 and 11 is shown in Figure D.0. a) and b). The maximum and minimum rates of change of all three occur at about the same time so that dP/dt is in fact a rough measure of the reaction rate. Figure D.0. c shows a plot of dP/dt against dMe_2CO/dt for Oxidations 1 - 5 at 273°. It shows that the proportionality factor is not sufficiently constant with variation of reactant composition to use dP/dt as a measure of the reaction rate.

4.3 Variation of kinetic parameters with reactant composition

In accordance with the results obtained in other studies of olefin oxidation,[93, 94, 115] the magnitude of kinetic parameters was strongly dependent upon reactant composition (Table C.24 Figures C.33 - C.34)

The overall pressure change (P_{∞}) decreased and the pressure decrease (P_{d}) increased as the ratio of fuel to oxygen in the system was increased. Over the pressure range tested at 303°, ΔP_{∞} came close to zero at fuel:oxygen pressure ratio of 200 : 100 mm. Hg. but the final pressure in the system did not become less than the starting pressure as it did with the same mixture at 273°. At low ratios of fuel to oxygen (40 : 100 mm. Hg.) ΔP_{∞} appeared to pass through a maximum (Figure C.33a), and under the same conditions the reaction showed no initial pressure decrease. Instead, a period of slow acceleration preceded the period of rapid pressure increase. Since analytical results showed that substantial quantities of products were formed early in the reaction, the latter condition is probably the result of an equilibrium between reactions producing a decrease in the number of molecules in the system and reactions yielding products responsible for a pressure increase i.e., carbon oxides and water.

The maximum rate of pressure increase, ($\rho_{max.}$), increased rapidly with increasing oxygen pressure from oxygen:fuel ratios 40 : 100 - 100 : 100 and then tailed off to apparent independence. The same was true when the reactant ratios were reversed, except that, at a pressure ratio

of about 100 : 100. ρ_{max} passed through a shallow maximum.

Since ρ_{max} has been shown to be a rough measure of the oxidation rate, (previous section), these results exhibit the tendency for excess olefin to inhibit the oxidation as was observed by other workers.

The ability of olefins to inhibit oxidations has been attributed to three possibilities:

a) the initial abstraction of a hydrogen atom from the fuel giving rise to a radical which may exist in resonance stabilised forms, for example with but-2-ene;

$$CH_3.CH{:}CH.CH_3 + O_2 \longrightarrow CH_3.CH \equiv CH \equiv CH_2 + HO_2 \quad \ldots (1)$$

b) under conditions of excess olefin pressure, where ΔP_∞ is less than the initial pressure, the decrease in the number of molecules in the system must be attributable to species more stable than peroxides, the likeliest possibility being polymers of the types mentioned in section E.4.1.(b).

c) olefins are known to inhibit the oxidation of aldehydes due probably to the replacement of the propagation step:

$$RCO_3 + RCHO \longrightarrow RCO_3H + R.CO \quad \ldots\ldots (2)$$

by $$RCO_3 + R'H \longrightarrow RCO_3H + R' \quad \ldots\ldots\ldots (3)$$

or $$RCO_3 + CH_2{:}CR_2 \longrightarrow R.CO.OO.CH_2.CR_2 \quad \ldots\ldots\ldots (4)$$

where R' is an alkyl radical.

Since the products of reactions (3) and (4) are likely to be less efficient chain carriers or branching agents than the carbonyl radical produced in (2) the olefin produces an inhibiting effect on the oxidation.

The maximum rate of pressure decrease, (ρ_d) became independent of oxygen at fuel to oxygen ratio 100 : 90 mm. Hg. but increased steadily over the range with increasing hydrocarbon pressure.

From Figure C. 35. the order of the reaction with respect to ρ_d gave an isobutene dependence of 1.4 (before the part of the range where ρ_d became independent of oxygen pressure). The corresponding values based on ρ_{max} gave an isobutene dependence of 0.7 and an oxygen dependence of 3.5

The effect of varying the total pressure of a 1 : 1 mixture showed that ΔP_d and ΔP_∞ rose slightly with increasing pressure, becoming independent of pressure at about 300 mm. Hg. ρ_d and ρ_{max} increased steadily over the range 100 - 300 mm. Hg.

Mixture of isobutene to oxygen of 200 : 100 mm. Hg. and 1 : 1 mixtures at 286 mm. Hg. and 373 mm. Hg. total pressure gave pressure pulses at approximately the time of the maximum rate of pressure increase, due presumably to the formation of cool flames, the rate of pressure change thereafter being much less than before the onset of the cool flame.

The effect of temperature and total pressure on the development of pressure/time curves of 1 : 1 mixtures is shown in Figure C. 31. The curves

showed all the characteristic properties already mentioned. The initial pressure decrease although small at all times was not completely removed until 352°.

The effect of coating the reaction vessel surface with boric acid was to speed up the reaction. Although there is no direct comparison between the runs in the boric acid vessel and that in a clean pyrex vessel, the run at 303° in the acid coated vessel at a total pressure of 100 mm. Hg. proceeded 25% faster than the run in a clean pyrex vessel at this temperature and twice this pressure and gave approximately the same overall pressure increase.

In potassium chloride and sodium hydroxide coated vessels the speed of the reaction was not greatly different from that in a clean pyrex vessel under the same conditions of temperature and pressure, indicating that the pyrex surface had naturally salt like properties. This was also borne out by the analytical results.

A further run in the sodium hydroxide coated vessel in which the 1 : 1 mixture of isobutene to oxygen was augmented by the addition of excess nitrogen (Oxidation No. 23) started off at a much faster rate exhibiting no initial pressure decrease. The maximum rate of pressure change was not reached until later in the reaction than was the case in the runs without added inert gas. That the maximum rate of pressure increase did not develop until later in the reaction may be due to the fact that the ratio of the fuel to

oxygen mixture was lower than before, (180 : 215 mm. Hg.), but the increase in the initial rate is most likely due to a lower destruction rate of HO_2 radicals since their passage to the reaction vessel walls will be hampered by the excess nitrogen. The net result would be an effective increase in the chain length and consequently a higher reaction rate.

5. Comparison with other systems

As stated earlier, the present experimental work was carried out in conjunction with a similar study on the oxidation of isobutane.

The initial stages of isobutane oxidation produced all the products observed in the olefin oxidation to a greater or lesser degree. The initial yield of the major product of the reaction, (isobutene), was affected only slightly by variation of oxygen pressure, an effect analogous to the slight variation of the initial yields of acetone in the isobutene oxidation. The yields of minor products varied greatly with reaction conditions. The initial yield of propylene for example passed through a maximum at high ratios of alkane to oxygen (4:1) and continued to decrease with increasing oxygen pressure. Although in the olefin oxidation experiments involving high ratios of fuel to oxygen were not practicable the general decrease in the initial yield of propylene with increasing oxygen pressure was reflected in this system. That the yield of an initial product of the oxidation should pass through a maximum with increasing oxygen pressure is extremely difficult to explain.

Similar trends in the yields of other minor products common to both systems were noted with isobutene oxide, methacrolein and acetaldehyde, although the yield of the latter increased much more sharply with increase in oxygen pressure in the alkane system.

Raising the temperature produced similar variations in the

yields of the same products in the two systems except isobutene oxide. The yield of the latter decreased with increasing temperature in the olefin system but increased five fold between 270° and 330° in the alkane oxidation. The initial yield of propylene increased by a factor of two between 270° and 300° and passed through a shallow maximum to give a lower yield at 330° while in the olefin oxidation the initial yield of this product increased steadily with increasing temperature. The initial yield of isobutene in the alkane oxidation was relatively unaffected by raising the temperature from 270° -330°.

Change of surface to boric acid produced roughly the same effect on the yields of minor products in both systems but in the potassium chloride coated vessels there was no obvious comparison between the product distributions in the two systems with the exception of the relative yields of acetaldehyde which in both cases were unchanged by changing from clean pyrex to potassium chloride.

The yields of minor products from the oxidation of isobutane, as from the oxidation of isobutene, could not be simply explained by a set of homogeneous reactions and verified that surface effects must play an important part in the formation of minor products.

6. Homogeneous and Heterogenous processes

So far reactions have been proposed which account for

a) the initial production of hydroperoxy radicals

b) homogeneous production of acetone and formaldehyde

c) low ratios of formaldehyde to acetone

d) variation of CO/CO_2 ratios with oxygen pressure,

by the following scheme:

$$CH_2{:}C(CH_3)_2 + O_2 \longrightarrow CH_2{:}C(CH_3)CH_2 + HO_2 \quad \ldots \quad (1)$$

$$(CH_3)_2.C{:}CH_2 + HO_2 \rightarrow (CH_3)_2.\underset{\displaystyle OOH}{\overset{|}{C}}\text{-}CH_2 \text{ or } (CH_3)_2C\text{-}CH_2OOH \quad \ldots (2)$$

$$(CH_3)_2.\underset{\displaystyle OOH}{\overset{|}{C}}\text{-}CH_2 \longrightarrow (CH_3)_2.CO + CH_2OH \quad \ldots\ldots\ldots \quad (3)$$

$$(CH_3)_2.C\text{-}CH_2OOH \longrightarrow (CH_3)_2.C.OH + CH_2O \quad \ldots\ldots\ldots \quad (4)$$

$$CH_2OH + O_2 \longrightarrow CH_2O + HO_2 \quad \ldots\ldots\ldots \quad (5)$$

$$(CH_3)_2C.OH + O_2 \longrightarrow Me_2CO + HO_2 \quad \ldots\ldots\ldots \quad (6)$$

$$CH_2OH + O_2 \rightarrow OO.CH_2OH \xrightarrow{\text{wall}} CO + H_2O + OH \quad \ldots\ldots\ldots \quad (7)$$

$$\xrightarrow[O_2]{\text{wall}} CO_2 + H_2O + HO_2 \quad \ldots\ldots\ldots \quad (8)$$

The problem now is to account for the variety of minor products and the variations in product distribution under different reaction conditions.

The experimental results outlined in previous sections have indicated that the nature of the reaction vessel surface is instrumental in determining

the distribution of minor products but sufficient evidence is not yet available to assess to what extent heterogeneous reactions occur and by what processes the minor products may be formed. Although the shapes of product development/time graphs (Figures C.1.-C.23) vary greatly over the range of conditions employed, the fact that the rates of production of major products are paralleled by the rates of formation of minor products suggests that minor product formation may be occurring via the same intermediate species as the major products.

The simplest possibility is that the initially formed C_4H_8OOH radicals formed by reaction (2) undergo two types of decomposition, a homogeneous decomposition producing major products and a heterogeneous reaction producing minor products. This sets up the following competition for C_4H_8OOH radicals:

$$C_4H_8 + HO_2 \rightarrow C_4H_8OOH \begin{cases} \rightarrow \text{Major Products} & \text{(A)} \\ \rightarrow \text{Minor Products} & \text{(B)} \end{cases}$$

where (A) homogeneous process

and (B) heterogeneous process

For such a scheme to operate the rate of homogeneous decomposition must be comparable with the rate of diffusion to the walls.

The mean diffusion for a molecule to reach the walls of a cylindrical vessel is given by Semenoff[1] on the basis of the Einstein diffusion equation:

$$t = d^2/32D$$

where t = Root mean square of the diffusion time

d = diameter of the vessel

D = diffusion coefficient.

The diffusion coefficient[154] of a small peroxy radical in a reaction mixture at 600°K and approximately 0.2 atmospheres pressure will be about 1 cm.^{2} sec.$^{-1}$ The reaction vessel had a diameter of 6 cm., so that the diffusion time may be approximately one second.

The rate constant for typical unimolecular decompositions can be given as:

$$k = A\exp(-E/RT)\ \text{sec.}^{-1}$$

where A is of the order of the collision frequency and may normally vary from 10^{12} - 10^{14}. The value may however be higher than 10^{14} if free rotation is introduced on the formation of the transition state. On the other hand, if a very rigid transition state is formed, A may be as low as 10^{11}.

The activation energy for the decomposition of a peroxy radical will be at least equal to the C - OOH bond strength which has been argued by Knox and Wells[117] to be about 25 k. cal. Before decomposition into reaction products the radical must undergo isomerisation so that the activation energy may be greater than 25 k. cal. mole.$^{-1}$ Kerr and Trotman-Dickenson[155] have shown that radical decompositions involving isomerisation probably require activation energies about 10 k. cal. mole^{-1} greater than decompositions which can be accomplished by simple bond breaking. A value of 35 k. cal. mole^{-1} might be reasonable for the decomposition of C_4H_8OOH in to products other than acetone and formaldehyde. Substituting this value in the equation above and taking $t = 1/k$ the lifetime of the radical is about 1 - 2 sec. at 600°K.

This rough measure of the rates of the two processes shows that the experimental ratios of major/minor products of approximately 4 : 1 are not

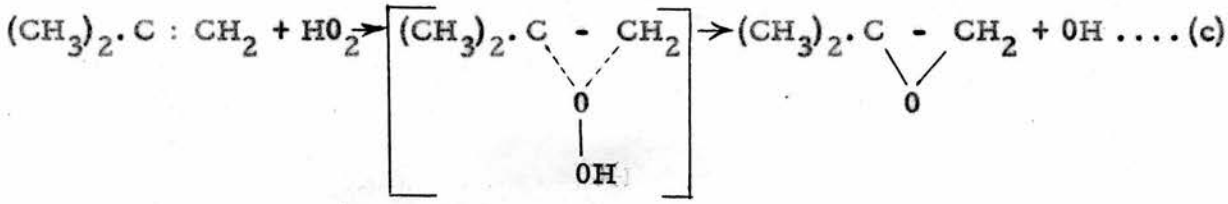
incompatible with a competition of this type.

Table D. 2 shows that the ratio of major/minor products decreases by a factor of two over the temperature range 246^0 - 352°, assuming carbon dioxide to be a minor product and not formed extensively by reaction (8). Over this range the pressure was decreased from 300mm. Hg. at 246° to 120 mm. Hg. at 352°. Since the diffusion coefficient $D \propto T^{3/2}/P$, the combination of increased temperature and decreased pressure will cause D to increase by a factor of three and hence cause a decrease in the ratio of major/minor products. However, increasing the temperature by 100° would have a much greater effect on reaction (A) than would the increased diffusion rate have on reaction (B).

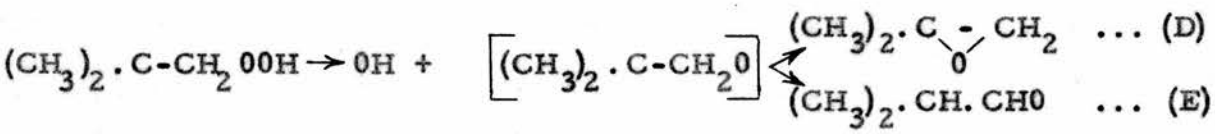
The situation need not be as clear cut as this. As the temperature is raised radicals will undoubtedly proceed to the walls at a faster rate but there will also be a greater chance of homogeneous unimolecular decomposition to products other than acetone and formaldehyde.

Measurement of the relative activation energies of reactions producing the various products showed that although some were too great to be considered as competing homogeneous processes, for example the reactions producing propylene and acetaldehyde, the activation energies of processes producing the other minor products were not greatly different from that producing acetone. In other words, at the lower temperatures minor products may be produced homogeneously to some extent but mainly by heterogeneous processes but as the temperature is increased the overall reaction may be more homogeneous with a greater proportion of the homogeneous reaction producing minor products. In the experiments at 273°

(Oxidations 1 - 5) the initial yield of isobutene oxide was not affected to nearly as great an extent as the initial yields of other minor products and an alternative homogeneous process for its production would be one similar to that proposed by Knox and Wells[117] for the formation of ethylene oxide in the oxidation of ethylene.



The initial yield of isobutene oxide decreased with increasing temperature. The decrease cannot be attributed to isomerisation of the oxide to isobutyraldehyde although the decrease in the yield of the oxide and the corresponding increase in the yield of aldehyde are apparently related. The change over from oxide to aldehyde cannot be easily explained by reaction (c) but the experimental result may be explained if a competition of the following type occurred:



Since process (E) requires an additional rearrangement of the diradical intermediate, one would expect this reaction to have a higher activation energy than reaction (D). With increasing temperature reaction (E) would be expected to occur to a greater extent and this may account for change from oxide to aldehyde as the temperature is increased.

The extent to which homogeneous and heterogeneous processes overlap as the temperature is increased is difficult to assess. However, at any one

particular temperature, the distribution of major/minor products would be purely diffusion controlled and the results from experiments conducted under conditions of varying reactant composition (Oxidations 1 - 5) did not support the idea of simple competition between homogeneous and heterogeneous processes. The ratio of major/minor products was relatively unaffected by varying the reactant pressure. Also, with mixtures of the same composition but total pressure decreased by a factor of two, the relative yield of minor products was not increased as would have been expected on the basis of a diffusion controlled process. The results from Oxidation No. 23, in which the reaction mixture pressure was augmented by the addition of excess nitrogen, did little to support or contradict the possibility of diffusion controlled reactions. The production of carbon dioxide which is almost certainly a heterogeneous process in a sodium hydroxide coated vessel (the inert gas experiment was carried out in a vessel of this type) became even greater with the mixture diluted with nitrogen.

The conflicting results obtained by varying the reactant pressure and adding inert gas did not on the whole support the possibility of a simple competition between homogeneous processes yielding major products and heterogeneous processes yielding minor products although the pressure variations applied were probably not great enough to fully test a diffusion controlled process.

At temperatures below 300° product formation starts at a maximum rate. From plots of product yields against extent of reaction (Figures D. 7 - D. 14) none of the products appears to undergo further attack until a late stage in the oxidation

and the reaction in this temperature range is not of the degenerately branching type. The rate of production of acetone is approximately first order with respect to both isobutene and oxygen pressure in this range. It is evident that the initiation process is therefore of greatest importance under these conditions since it appears to be the only source of radicals starting new chains. If reaction (1) were the sole initiation process, the fate of the C_4H_7 radicals formed by hydrogen abstraction is of interest. At early stages in the reaction, the most likely fate would be oxidation to the corresponding peroxy radical:

$$CH_2:C(CH_3).CH_2 + O_2 \rightarrow CH_2:C(CH_3).CH_2OO$$

The peroxy radical could then either abstract a hydrogen atom to form the corresponding hydroperoxide or else decompose as follows:

$$CH_2:C(CH_3).CH_2OO \longrightarrow CH_2:C(CH_3).CHO + OH$$

Formation of a hydroperoxide would not be expected to be an important reaction since Kirk and Knox[55] have shown that these compounds have only a short life at about 300°. If the hydroperoxide did have a fleeting existence, however, methacrolein would probably still be produced by dehydration of this species:[109]

$$CH_2:C(CH_3).CH_2OOH \longrightarrow CH_2:C(CH_3).CHO + H_2O$$

The ratio of acetone to methacrolein would then give a rough measure of the maximum possible chain length. At the lower temperatures where the greater proportion of C_4H_8OOH radicals are considered as producing major products, the ratio of acetone to methacrolein under these conditions was about forty to one.

Before further consideration is given to possible modes of formation of products, it is as well at this stage to consider alternative reactions open to the

radicals postulated in the reaction schemes so far. The fate of hydroperoxy, isopropyl and isobutenyl radicals have been dealt with already in this and other sections. The concentrations of hydroxymethylene and C_4H_8OOH may be reasonably high in the system. Recombination or isomerisation of hydroxymethylene would yield ethylene glycol or methoxy radicals. Avramenko and Kolesnikova[156] showed that the radical produced by attack of hydrogen atoms on methyl alcohol, which they accepted as being CH_2OH, underwent oxidation to formaldehyde as in reaction (5) above with an activation energy of 2.5k. cal. $mole^{-1}$. They found no evidence of recombination of hydroxymethylene to ethylene glycol except in the absence of oxygen. The isomerisation of hydroxymethylene to methoxy would, therefore, require a much greater activation energy than would its oxidation. In the early stages of reaction, processes other than oxidation need not be considered as important.

In the case of C_4H_8OOH the position is not so clear. If most of the products arise from destruction of C_4H_8OOH a rough measure of the concentration of this radical can be made. The rate of production of products is about 2.5×10^{-6} mole l^{-1} $sec.^{-1}$ at 293° and if the removal time of C_4H_8OOH either by homogeneous or heterogeneous destruction is approximately one second then:

$$\left[C_4H_8OOH\right] \approx 2.5 \times 10^{-6} \text{ mole } l^{-1}$$

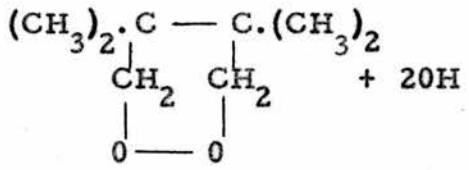
The rate of recombination of radicals given by:

$$2C_4H_8OOH \xrightarrow{k_r} \text{Inert products}$$

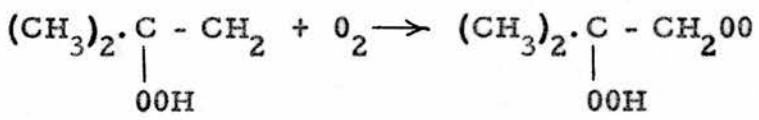
will be $6.3 \times 10^{-12} k_r$ mole l^{-1} sec.$^{-1}$ The rate constant for the recombination in the gas phase of large hydroperoxy radicals is not known. For the recombination to be important compared to unimolecular decomposition k_r would have to be 10^5 mole^{-1} l. sec.$^{-1}$ The activation energy for the recombination of radicals is low and if the A factor were of the order of that for the recombination of small alkyl radicals, i.e. 10^{11} mole^{-1} l. sec.$^{-1}$ a rate constant of 10^5 mole^{-1} l. sec.$^{-1}$ would involve a steric factor of 10^{-6}. The analogy with small alkyl radicals may not, however, be justified. Two large radicals such as C_4H_8OOH would have to be favourably orientated to facilitate recombination. This would be less easily accomplished than with, for example, methyl or ethyl radicals and may well result in a steric factor several powers of ten lower than that for alkyl radicals, the steric factors in this case being of the order of 10^{-3}. With so little knowledge of the behaviour of large radicals, however, recombinations of C_4H_8OOH to produce molecules of the type:

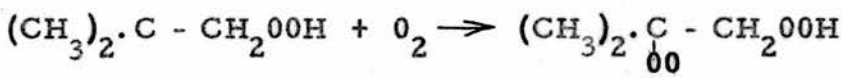
$$(CH_3)_2.C - C.(CH_3)_2 \qquad CH_2 - CH_2 \qquad (CH_3)_2.C - CH_2$$
$$\quad | \quad | \qquad\qquad\quad | \quad | \qquad\qquad\quad | \quad |$$
$$H00.CH_2CH_2OOH \qquad H00.C(CH_3)_2 \quad C(CH_3)_2.OOH \qquad H00.CH_2C(CH_3)_2OOH$$

cannot be discounted. Hydroperoxides of this type would be unstable at 300° and would quickly decompose to give, for example:

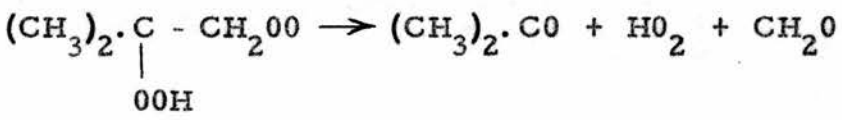


If combinations of the type above are important, then due to the free radical nature of the oxygen molecule, peroxyradicals of the following types would be expected:

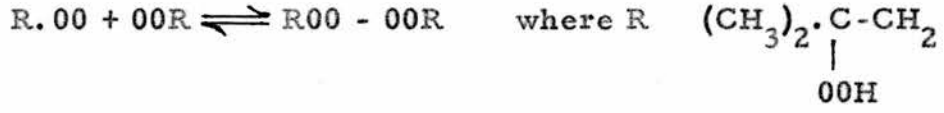




This reaction is similar to that postulated by Skirrow and Williams[94] and is of a type previously suggested by Cartlidge and Tipper[54]. The highly oxygenated radical produced would be liable to the same reaction as C_4H_8OOH. Homogeneous decomposition would yield acetone and formaldehyde:



while heterogeneous destruction may account for the production of minor products. Recombination would not be expected to be an important reaction with this radical since the 0-0 bond would be weak



and the dimer would be likely to dissociate again to peroxy radicals or to a substituted alkoxy plus oxygen:

$$R.00 + R.00 \rightarrow 2RO + O_2$$

In liquid phase oxidations chain termination processes by radical recombination have steric factors of the order of 10^{-6} and, since as low a value as this is not likely in the gas phase,[157] the formation of peroxy radicals of the type outlined above seems a reasonable alternative to chain termination by recombination.

An alternative fate of the R.00 radicals would be addition to another fuel molecule[128]:

$$HOO.C_4H_8 + O_2 \rightarrow HOO.C_4H_8.OO \xrightarrow{C_4H_8} HOO.C_4H_8.OO.C_4H_8$$

Provided addition of oxygen to the radicals is faster than addition of radicals to fuel molecules chains of this type may be set up with alternate addition of oxygen and isobutene to the original hydroperoxy radical. Just how far the chains will continue for will depend on how unstable the peroxy polymers are. At temperatures around 300° one would not expect large radicals of this type to be very stable,[158] and homogeneous decomposition at any stage would give major products of the reaction. If, however, the energy of each successive addition were absorbed by the large radicals some of the chains may continue for several additions. In this case some of the polymers may reach the wall before homogeneous decomposition occurs and the heterogeneous fragmentation of the large radicals could account for the production of the minor products. The same limitations must be placed on this type of mechanism as on the simple homogeneous/heterogeneous competition outlined previously.

Although the formation of products by the polymerisation mechanism need not be diffusion controlled, as the temperature is increased the rate of unimolecular decomposition of the radicals will become greater and the length of the chains smaller. One would therefore expect the ratio of major/minor products to increase with increasing temperature whereas the opposite is the case. In order to explain the experimental results by such a scheme it must be assumed that as the temperature is increased the reaction takes place homogeneously to a greater extent and that a greater proportion of the radicals produce minor products by homogeneous processes.

It is obvious that a simple mechanism involving a common intermediate species and involving both homogeneous and heterogeneous processes cannot satisfactorily account for the experimental results without making some assumptions the validity of which is questionable. If direct competition between gas phase and wall reaction, the polymerisation processes are to be avoided, one must consider a reaction mechanism whereby major and minor product formation occurs by two different types of reaction.

A four centre type reaction may occur which could account for the production of major products:

$$(CH_3)_2.C{:}CH_2 + HO_2 \rightarrow \left[(CH_3)_2.C\begin{array}{l}\text{-}CH_2\\ \vdots\\ O\cdots O\text{-}H\end{array}\right] \rightarrow (CH_3)_2.CO + CH_2OH \quad \ldots . (F)$$

or

$$\left[(CH_3)_2.C\begin{array}{l}\text{-}CH_2\\ \vdots\\ H\text{-}O\cdots O\end{array}\right] \rightarrow (CH_3)_2.C.OH + CH_2O \quad \ldots . (F')$$

$$(CH_3)_2.C{:}CH_2 + HO_2 \rightarrow (CH_3)_2.C - CH_2OOH \xrightarrow{wall} \text{Minor Products} \ldots (B)$$

followed by oxidation of the resulting radicals as before. The minor products may then arise by heterogeneous destruction of C_4H_8OOH radicals formed by addition of hydroperoxy to the double bond of isobutene molecules. If the hydroperoxy radical were sufficiently unreactive that it need not decompose on its first few collisions with the wall, the formation of minor products will not be diffusion controlled, and the ratio of major/minor products would not be affected by varying the reactant composition or on the addition of inert gas. If the activation energy of reaction (B) were greater than that of reaction (F) this would also explain the decrease in the ratio of major/minor products with increasing temperature. However, the concentration of C_4H_8OOH radicals would still be reasonably high and the rate of recombination comparable with the rate of diffusion. If the hydroperoxy radical were further oxidised to $HOO.C_4H_8.OO$ and this radical lived long enough to reach the wall, this could lead to the heterogeneous formation of minor products.

The main objection to a mechanism of this type is that the difference between the two modes of attack by HO_2 on the fuel may be considered to be too fine to produce such drastically different results especially since addition of HO_2 to the double bond to form a hydroperoxy radical would be expected to have a low activation energy and would be the more likely reaction to occur. One would expect the simpler reaction to account for the production of major products.

A discordant feature of the results is that the activation energies for the reactions producing minor products are greater than for that producing acetone. If the minor products were produced solely by heterogeneous processes one would expect the effective activation energies for their production to be decreased and as the temperature is raised the production of major products should become the more important process. In order to incorporate this anomaly in the proposed scheme of homogeneous and heterogeneous processes it must be assumed that as the temperature is increased the whole reaction becomes progressively more homogeneous and in effect the activation energy differences measured at higher temperatures were of virtually homogeneous processes. This may to some extent account for the break in the relative activation energy curves at about 300° (Figure D.33).

It is also of interest to inspect in more detail the difference in the two types of reaction which occur above and below 300°.

It has been shown that the rate of formation of acetone is dependent to the same extent on isobutene and oxygen pressures, the order below 300° being about one in each case. Since product development starts at a maximum rate for all products below 300° an oxygen and isobutene dependence of this order for the production of acetone on the basis of reactions 1 - 3 (page 191) could be reasonably explained.

Initiation processes are generally accepted as being heterogeneous which leads to an effective reduction in the activation energy of this process. Although the initiation process may, therefore, have a small or zero

activation energy the fuel and oxygen molecules will have to be favourably orientated on the surface of the reaction vessel before reaction occurs and reaction (1) may well be a slow process. Reaction (2) will also have a low activation energy but since the reaction is homogeneous it will occur at a faster rate than (1). The decomposition of C_4H_8OOH to acetone and hydroxymethylene will require an activation energy[117] of about 25 k. cal. $mole^{-1}$. In fact, the activation energy of the process, calculated from the initial rates of formation of acetone in Oxidation Nos. 1 - 4 was 27 k. cal. $mole^{-1}$. Such a high value for the activation energy suggests that reaction (3) would not be a fast reaction and the dependence of the rate of formation of acetone on isobutene and oxygen pressure can be explained in two ways:

a) Reaction (1) may be the rate determining step i. e. reaction (1) is slower than reaction (3).

or b) Reaction (3) may be the rate determining step and the rate of production of hydroperoxy radicals is first order in oxygen pressure and zero order in isobutene pressure.

Either of the above processes would account for the experimental order observed for the rate of production of acetone. If condition b) were the case, however, there would be a build up in the concentration of C_4H_8OOH radicals. Such a condition would lend itself to chain termination by recombination of C_4H_8OOH radicals. Since the recombination would have a very low activation energy compared to the homogeneous decomposition of the radicals, the relative yield of acetone should increase with increasing temperature, whereas the opposite is the case. With condition a), however,

the hydroperoxy radicals would be used up quickly in propagating the chain and recombination or radical destruction would be less important.

If condition a) did in fact operate, the kinetics of the reaction would be strongly dependent upon the initiation process below 300° where there is no evidence of branching reactions occurring. Also, the fact that the rate of formation of acetone is first order in both isobutene and oxygen pressure suggests that the chains may be short as has been already suggested.

As the temperature is increased above 300°, the pressure was correspondingly decreased so that the rate of reaction (1) would be decreased due to the lower concentration of isobutene and oxygen and with increasing temperature the fuel and oxygen molecules will be desorbed from the surfaces to a greater extent decreasing further the rate of production of hydroperoxy radicals. At temperatures above 300°, however, it has been shown that the isobutyraldehyde produced in this region is oxidised at a fast rate thereby producing hydroperoxy radicals by branching reactions:

$$(CH_3)_2.CH.CHO + O_2 \rightarrow (CH_3)_2.CH.CO + HO_2$$

$$(CH_3)_2.CH.CO \rightarrow (CH_3)_2.CH + CO$$

$$(CH_3)_2.CH + O_2 \rightarrow CH_3.CH{:}CH_2 + HO_2$$

In this temperature range, therefore, the emphasis shifts from the initiation process to the branching reactions. Since the main supply of fuel attacking radicals now comes from a molecular intermediate, this would explain why the reaction becomes autocatalytic at the higher temperatures. The high activation energy of reaction (3) means that this process will become relatively more important as the temperature is increased and result in a

faster production of hydroperoxy radicals by reaction (5).

The fact that the ratio of the yields of acetone to the minor products (except isobutene oxide) decreases as the temperature is increased suggests that the minor products may be produced by homogeneous processes having higher activation energies than that producing acetone rather than by heterogeneous processes. The effect on the initial yields of products of varying the reaction conditions and the high activation energy differences in some cases between what would be competing homogeneous processes, however, makes an overall reaction comprising essentially homogeneous processes as difficult to accept as the exact nature of the heterogeneous reaction is to explain.

Conclusion

Reference has been made throughout the text to particular points from the published work of other workers on the slow combustion of olefins. It is now of interest to summarise the results from the present oxidation and to see how well they fit the pattern of previous studies.

a) Pressure/time curves were obtained which exhibited a characteristic sigmoid shape although, below 300°, the reaction was not of the degenerately branching type and it was only at temperatures above 300° that the reaction became autocatalytic in nature.

b) Under suitable conditions of temperature and pressure, pressure pulses were observed due to the formation of cool flames.

c) Major products of the reaction were formed by apparently homogeneous reactions resulting from attack on the double bond, presumably by a radical species, while the formation of minor products was difficult to account for.

d) Peroxides were barely detectable in the reaction products.

e) Variations of kinetic parameters with reaction conditions were remarkably similar to thoseobtained by Skirrow and Williams from oxidation of the same olefin. That the

two systems should be consistent in this respect is even more remarkable since the kinetics of olefin/oxygen systems have no obvious interpretation.

As far as these points of agreement are concerned the present oxidation conformed to a type of reaction variously postulated as being essentially homogeneous and should, therefore, be subject to the homogeneous radical decomposition theories of the time.

In spite of conforming to the general pattern of olefin oxidations, a much more comprehensive investigation of the reaction has shown that the present oxidation theories of homogeneous radical decomposition may be suspect. The reaction vessel surface plays an active part not only in the kinetics of the reaction but in the distribution of products and more particularly in the formation of minor products of the reaction. This has been confirmed by measurements of relative activation energies of reactions producing major and minor products, the differences in some cases being too great to uphold the theory of completely homogeneous decomposition of intermediate radicals.

It is difficult to see how the mechanisms of the oxidations of higher hydrocarbons can be satisfactorily elucidated by studies in static systems unless a reaction vessel with completely inert walls can be devised. The immediate future for slow combustion studies would appear to lie in

flow system experiments where experimental conditions can be regulated to ensure that reactive radical species react homogeneously without having time to diffuse to the walls. The introduction of known radical species into the system may also go some way to explaining the course of the reaction.

Although the introduction of gas chromatography has allowed a much closer inspection of the molecular species formed in the early stages of oxidation, the exact nature of the reactions occurring will not be completely known until an experimental technique is devised which will allow analysis of the small quantities of radicals present.

Summary

A study has been made of the slow combustion of isobutene in a static system. The reactions were carried out initially in a pyrex glass reaction vessel. Comprehensive product analysis was carried out almost entirely by gas chromatography. The effect on the product distribution of varying the ratio of oxygen:isobutene pressure over a four fold range and of varying the ratio of isobutene:oxygen pressure over the same range was studied at 273°. Similarly, the product distribution was determined for the oxidation of 1:1 mixtures of isobutene:oxygen at a series of temperatures in the range 246° - 352°. Relative activation energies of the reactions producing many of the products were determined.

The early stages of the oxidation produced acetone and formaldehyde as the major products, the two accounting for about 70% of the carbon consumed at low conversions of isobutene. The major products were produced by an apparently homogeneous process involving attack on the olefinic bond of the fuel molecule. A reaction mechanism has been proposed for the formation of acetone and formaldehyde by homogeneous breakdown of intermediate C_4 hydroperoxy radicals formed by addition of hydroperoxy to isobutene.

The wide variation of the initial yields of the variety of minor products of the reaction could not be explained on the basis of present day theories of slow combustion. The effect on the product distribution of

varying the nature of the reaction vessel surface was studied by carrying out oxidations in vessels coated with a range of inorganic materials from acidic to basic.

Although the reaction appeared to be of a free radical nature and the pressure/time curves were of a characteristic sigmoid shape, there was no evidence of branching reactions below 300° and products were produced initially at a maximum rate. Above this temperature the product development assumed a more autocatalytic form which has been supposed as being due to oxidation of isobutyraldehyde which was an initial product in this temperature range.

It has been proposed that contrary to general belief the nature of the reaction vessel surface is instrumental in controlling the formation of minor products and that they are produced by heterogeneous decomposition of oxygenated radical species.

The appearance of isobutene oxide and isobutyraldehyde in the reaction products necessitated a separate study of the isomerisation of isobutene oxide to ascertain whether isobutyraldehyde was a legitimate product of the oxidation or formed by isomerisation of the epoxide.

The kinetics of the oxidation were studied at 303° and the variation of kinetic parameters, although still largely unexplained, was found to be in reasonable agreement with the results obtained from previous kinetic studies carried out on the same hydrocarbon.

Several simple reaction mechanisms involving homogeneous and heterogeneous processes have been discussed to illustrate that the relationship between the reaction vessel surface and the formation of minor products is not a simple one.

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